Conversion and Residence Time Calcula-tion for Gas-solid Solid Reactions of the Cylindrical-shaped Particles with Con-stant Size Using the Shrinking Core Model

Mohammad Reza Talaghat* and Ehsan Zangooei

Department of Chemical Engineering, Oil and Gas, Shiraz University of Technology

Abstract

In this paper, a mathematical model is developed to calculate the conversion and the residence time reaction for plug flow and mixed flow in the reactors filled with cylin-drical particles using the shrinking core model. In this modeling, the size of the particles is un-chamged during the reaction. Also, the reaction rate is controlled by the gas layer resistance, the ash layer resistance, and the reaction resistance as well as the combination of them. In addition, it is assumed that the gas diffuses radially from the side, whereas the effect of diffusion in the axial direction is neglected. Equations are solved by numerical methods. It can be said that the innovation of this paper is the study of the effect of combination of resistances on the conversion of the reaction. Model evaluation shows that the results of modeling have a good consistency with the experimental data. The results show that at a certain time, when the rate of reaction is controlled by each of the resistances individually, the conversion rate is greater when the reaction is controlled by the ash layer resistance than when it is controlled by the other two resistance regimes. Finally, the effect of the combination of different controlling regimes on the conversion and residence time of reaction for plug flow and mixed flow of particles is studied and it is found that the overall results are similar to each other.

1. Introduction

We should clearly understand that every conceptual picture or model for the progress of reaction comes with its mathematical representation, i.e., its rate equation. Consequently, if we choose a model, we must accept its rate equation and vice versa. If a model corresponds closely to what really takes place, then its rate expression will closely predict and describe the actual kinetics; if a model differs widely from reality, then its kinetic expressions will be useless. We must remember that the most elegant and high-power mathematical analysis based on a model which does not match reality is worthless for the engineer who must make design

* Corresponding Author.
Tel./Fax: +987137354520
Email address: talaghat@sutech.ac.ir (M.R. Talaghat)

predictions. The requirement for a good engineering model is that it should be the closest representation of reality, which can be treated without too many mathematical complexities. For the non-catalytic reaction of particles with surrounding fluid, we consider two simple idealized models, the progressive-conversionmodel (PCM) and the shrinking unreacted-core model (SCM) [1-3]. In progressive conversion model, gas enters and reacts throughout the particle at all times, most likely at different rates and at different locations within the particle. Thus, solid reactant is converted continuously and progressively throughout the particle as shown in Fig. (1).
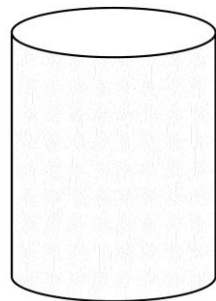

Figure 1. Cylindrical particle shape

In the shrinking core model, the reaction occurs first at the outer skin of the particle. The zone of reaction then moves into the solid, leaving completely converted material and inert solid behind. We refer to these as "ash." Thus, at any time, there exists an unreacted core of material, which shrinks in size during the reaction as shown in Fig. (2).

The shrinking core model is perfectly simple and more consistent with reality; observations about parts burning wood and coal confirm the validity of this model. The solid material is completely converted to ash, which remains when reaction of products is not gaseous, during the progress of the reaction. At this case, film diffusion, ash diffusion, and reaction are controlled. In slicing and examining the cross section of partly reacted solid particles, we usually find unreacted solid material surrounded by a layer of ash. The boundary of this unreacted core may not always be as sharply defined as the model pictures it; nevertheless, evidence from a wide variety of situations indicates that in most cases, the shrinking-core model (SCM) approximates real particles more closely

than the progressive conversion model (PCM) does. Observations with burning coal, wood, briquettes, and tightly wrapped newspapers also favor the shrinking-core model. Since the SCM seems to reasonably represent reality in a wide variety of situations, we develop its kinetic equations in the following section. In doing so, we consider the surrounding fluid to be a gas. However, this is done only for convenience, since the analysis applies equally well to liquids [4-7].
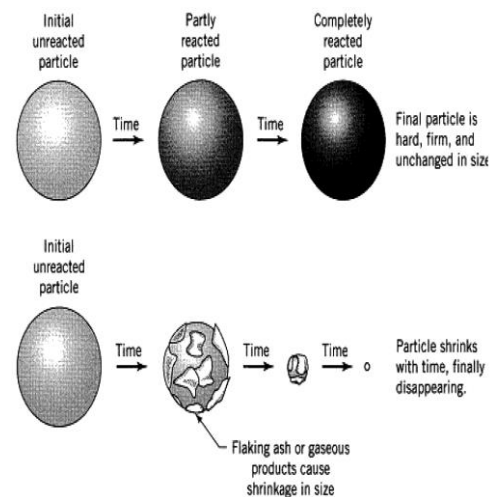

Figure 2. Different sorts of behavior of reacting spherical solid particle using the shrinking core model [1]

In this paper, the conversion and residence time of reaction for cylindrical particles of unchanging size during the gas – solid reaction is modeled using the shrinking core model. There are a few works in literature concerned with mathematical modeling of gas – solid reaction [1-7]. However, the following cases are not considered in these works:

i) The development of a model for the case the chemical reaction rate is controlled by the combination of resistances and its effect on conversion and residence time of reaction.

ii) The effect of plug flow and mixed flow of particles on the conversion and residence time of reaction.

2. Mathematical Modeling

For a general reaction, involving both solid and gas phases in both reagents and products, the

physical steps concerning the gas in the process are the following [8]:

- Transfer within the external gas to the surface of the pellet.
- Diffusion through the intergranular pores.
- Adsorption into the solid reacting phase.
- Desorption of the produced gas.
- Diffusion of the product gas to the external particle surface.
- Diffusion of gaseous products through the gas film back into the main body of fluid.
- Transfer of the produced gas from the particle surface to the bulk gas.

Each of these steps has its own kinetics and can limit, also in part, the overall rate of conversion. In some situations, some of these steps do not exist. For example, if no gaseous products are formed, steps 4 and 5 do not contribute directly to the resistance to the reaction. Also, the resistances of the different steps usually vary greatly. In such cases, we may consider the step with the highest resistance to be rate-controlling. The process can be successfully described as a chemical regime, when a surface process controls the overall kinetics, or as a diffusional regime, when the rate is determined by diffusion, or as a mixed regime [1-3].

In the literature, in many cases, some simplifications are assumed in order to formulate models that are applicable to the description of full-scale reactors as much as possible. A very comprehensive, classical treatment of the subject can be found in the seminal book of Szekely [9]. In spite of the impact, the quantitative treatment of reactive solids predominantly remains based on an oversimplification of the actual physics that can be extremely complicated by the already mentioned issues. A more simplified approach assumes non-porous particles [10] or non-porous shrinking core model (SCM) [11]. According to it, the reaction is supposed to take place only on a surface separating the unreacted core by the product layer in the particle, and moving to the center as the reaction goes on. This physical description is not always correct and, in general, it is not predictable whether or not a gas-solid reaction occurs by forming a core-shell structure as it depends on the reaction conditions (structure and size of the particle, temperature, pressure, composition of the feed gas, etc.). Even with this limitation, the SCM is still widely used [12-17] as

it provides a simple analytical solution to most cases, and it can still account for the presence of mass transfer resistances inside and outside the reacting solid, even if in a simplified way.

Consider a solid particle, where a single gas-solid reaction occurs, in the form:

$$A(Gas) \longrightarrow bB(Solid) \quad Product$$
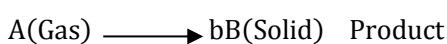
One simple way of describing the reaction of a solid particle with a gas is using the shrinking core model. The main assumption of this model is that the reaction develops topochemically only on a single surface, which separates two zones within the solid. The unreacted core is made of pure solid reagent, which has not been reached by the reacting gas yet, and a reacted outer layer is made of the pure solid product, which is porous and where the gas diffuses but does not react, because the solid matrix is completely inert. The core-shell interface moves inward, as long as the core is consumed, and the shell becomes thicker. This concept can be applied to different particle geometries.

For cylindrical pellets, the core-shell interface is a cylindrical surface concentric with the external one. In this modeling, according to Fig. (1), for a cylinder, it is assumed that the gas diffuses radially from the side, whereas the effect of diffusion in the axial direction is neglected. This means that the model is more accurate if the radius of the particle is much smaller than its height. This assumption allows for considering a one-dimensional problem. One advantage of assuming a core-shell type reaction is that the global conversion of the single particle is simply related to the position of the core-shell interface [2, 6]. The conversion is in fact defined as:

$$x_B(t) = \frac{n_B(0) - n_B(t)}{n_B(0)} \tag{1}$$

where n_B is the number of moles of the reagent solid into the particle. If the reagent is present only in the core, then the amount of reagent in the particle is linearly related to the volume of the core via the reagent density:

$$n_B(t) = \frac{\rho_{Bc}}{MW_{Bc}} V_{Bc} \tag{2}$$

Thus, combining Eqs. (1) and (2), the particle conversion is:

$$x_B = 1 - \frac{V_{Bc}(t)}{V_{Bc}(0)} \tag{3}$$

For this particle, the surface area (S_B) and the volume (V_B) of the particle are obtained using Eqs. (4) and (5) for a particle at initial time and Eqs. (6) and (7) at t (or for unreacted core), respectively:

$$S_B = 2\pi RL \tag{4}$$

$$V_B = \pi R^2 L \tag{5}$$

$$S_{Bc} = 2\pi r_{Bc} L \tag{6}$$

$$V_{Bc} = \pi r_{Bc}^2 L \tag{7}$$

where L is the length, r_{Bc} is the radius of unreacted core, and R is the original cylindrical pellet. Eq. (3), as a function of the pellet radius, is obtained by the following equation:

$$x_B = 1 - (\frac{r_{Bc}}{R})^2 \tag{8}$$

The system of equations for the gas and solid can be easily solved by considering a number of possible simplifications. In this research, we use the rate-controlling step for analysis, because the resistances of the different steps usually vary greatly. In such cases, we may consider the step with the highest resistance to be rate-controlling.

In this treatment, we develop the conversion equations for cylindrical particles, for which the steps:

1. Diffusion of gaseous reactant A through the film surrounding the particle diffusion;
2. Penetration and diffusion of A through the blanket of ash to the surface of the unreacted core; and
3. Reaction of gaseous A with solid at this reaction surface

We then extend the analysis to situations where the combined effect of these three resistances must be considered [1, 4-6].

2.1. Diffusion through gas film layer

Whenever the resistance of the gas film is controlled, no gaseous reactant is present on the particle surface; hence, the concentration driving force C_{Ag} - C_{As}, becomes C_{Ag} and is constant at all times during reaction of the particle. Now, since it is convenient to derive the kinetic equations based on available surface, we focus on the unchanging exterior surface of aparticle S_{ex}. From the stoichiometry of Eq. (1), we get:

$$dN_B = bdN_A \tag{9}$$

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt} = -\frac{1}{2\pi RL}\frac{dN_B}{dt} =$$

$$-\frac{b}{2\pi RL}\frac{dN_A}{dt} = bk_g(C_{Ag} - C_{As}) \tag{10}$$

$$= bk_g C_{Ag} = \cos\tan t$$

where k_g is the mass transfer coefficient between fluid and particle.

Where C_{Ag} is concentration of A in the gas phase, C_{As} is concentration of A on the unreacted core surface and k_g is the mass transfer Lcoefficient between fluid and particle. et ρ_B be the molar density of B in the solid and V be the volume of aparticle; the amount of B present in a particle is:

$$N_B = \rho_B V_B = (\frac{molesB}{m^3 solid})(m^3 solid) \tag{11}$$

then,

$$-dN_B = -bdN_A = -\rho_B dV_B = -\rho_B d(\pi r_c^2 L) = -2\pi\rho_B r_c dr_c \tag{12}$$

Replacing Eq. (12) in Eq. (10) gives the rate of reaction in terms of the shrinking radius of the unreacted core, or:

$$-r_B = -\frac{1}{S_{ex.}}\frac{dN_B}{dt} = -\frac{1}{2\pi RL}\frac{2\pi\rho_B Lr_c dr_c}{dt}$$

$$= -\rho_B \frac{r_c dr_c}{R dt} \tag{13}$$

Rearranging and integrating, we find how the unreacted core shrinks with time:

$$t = \frac{\rho_B R}{2bk_g C_{Ag}}(1 - (\frac{r_c}{R})^2) \tag{14}$$

Let the time for complete conversion of a particle be τ . Then, by taking $r_c = 0$

in Eq. (14), we find:

$$\tau_f = \frac{\rho_B R}{2bk_g C_{Ag}} \tag{15}$$

The radius of unreacted core in terms of fractional time for complete conversion is obtained by combining Eqs. (14) and (15):

$$\frac{t}{\tau_f} = 1 - (\frac{r_c}{R})^2 \tag{16}$$

Using Eq. (8), this equation can be written in terms of fractional conversion:

$$\frac{t}{\tau_f} = X_B \tag{17}$$

The contact time or reaction time needed for any specific conversion of solid in the plug flow is the same for all particles. Therefore, for a particle or number of particles, the conversion is the same and found directly from Eq. (17) for the gas film diffusion in controlling step [6-9].

Consider a solid feed consisting a mixture of different-size particles. Size distribution of this feed can be represented either as a continuous distribution or as a discrete distribution.

Let F be the quantity of solid being treated in unit time. Since the density of solid may change during the reaction, F is defined as the volumetric feed rate of solid in the general case. Where density change of the solid is negligible, F can represent the mass feed rate of solid as well. In addition, let $F(R_i)$ be the quantity of material of size about R_i fed to the reactor. If R_m is the largest particle size in the feed, we have for particles of unchanging size:

$$F = \sum_{R_i}^{R_m} F(R_i) \tag{18}$$

when in plug flow all solids stay in the reactor for the same length of time t_p. From this and the kinetics for whatever resistance controls, the conversion $X_B(R_i)$ for any size of particle R_i can be found. Then, the mean conversion X_B of the solids leaving the reactor can be obtained by properly summing to find the overall contribution to the conversion of all sizes of particles. Thus:

$$1 - \overline{X}_B = \sum_{R(t_p = \tau)}^{R_m} [1 - X_B(R_i) \frac{F(R_i)}{F} \tag{19}$$

where $R(t_p = \tau)$ is the radius of the largest particle completely converted in the reactor.

For the mixed flow of a single particle, conversion depends on the residence time in bed and residence time of each particle is different. Thus, the mean conversion of solid particles must be used:

$$1 - \overline{X}_B = \int_0^{\tau_A} (1 - X_B) E dt \tag{20}$$

where E is the exit age distribution of the solids in the reactor. For the mixed flow of solids, the residence time is calculated as follows:

$$E = \frac{1}{\bar{t}} e^{-\frac{t}{\bar{t}}} \tag{21}$$

Replacing Eq. (21) in Eq. (20) gives:

$$1 - \overline{X}_B = \int_0^{\tau_A} (1 - X_B) \frac{1}{\bar{t}} e^{-\frac{t}{\bar{t}}} dt \tag{22}$$

For gas film controlling step, replacing Eq. (17) in Eq. (22) gives the mean conversion as the following equation [1]:

$$\overline{X}_B = 1 - \frac{\tau_f - \bar{t}}{\tau_f} - \frac{\bar{t}}{\tau} e^{-\frac{\tau_f}{\bar{t}}} \tag{23}$$

The above conversion-time expressions assume that single resistance controls throughout reaction of the particle. However, the relative importance of the gas film, ash layer, and reaction steps will vary as particle conversion progresses. For example, for a constant-size particle, the gas film resistance remains unchanged; the resistance to reaction increases as the surface of unreacted core decreases; and the ash layer resistance is nonexistent at the start because no ash is present, but becomes progressively important as the ash layer builds up. In general, then, it may not be reasonable to consider that just one step controls throughout the reaction. The conversion and residence time for cylindrical-shaped particles of constant size is calculated for film diffusion controls, ash diffusion controls, chemical reaction controls, and the combination of them.
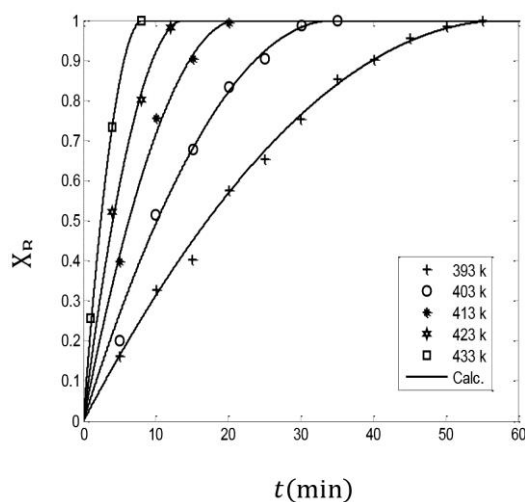
3. Results and Discussion

In this paper, the mathematical modeling is developed to calculate the reaction conversion and residence time for both plug flow and mixed flow in the reactors filled with cylindrical particles using the shrinking core model. In this modeling, the size of the particles is fixed and will not change during the reaction. Also, the chemical reaction rate is controlled by the gas film layer resistance, the ash layer resistance, and the chemical reaction resistance as well as the combination of them.

These results are shown in Tables (1) and (2). For evaluation of this modeling, the results of the model are compared with corresponding experimental data. The comparison between the mathematical modeling results and experimental data at various temperatures is shown in Fig. (3). The experimental data from the reaction of anthraquinone and sodium sulfide is obtained in an alkaline environment [10].
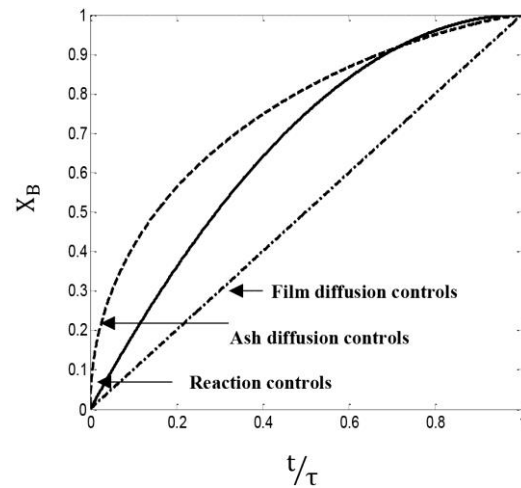
It can be seen in this figure that the results of the model have a good consistency with the experimental data. In addition, according to this figure, by increasing the reaction temperature, the conversion of reaction increases. The result of conversion versus time for a plug flow in the reactor filled with cylindrical particles is given in Fig. (4).

Table 1. Conversion-time expressions for plug and mixed flows

Combination of film diffusion, ash Diffusion, and reaction controls	$t_t = t_f + t_A + t_r$ $t_t = \tau_f X_B + \tau_A[(1-X_B)\ln(1-X_B)+X_B] + \tau_r\left[1-(1-X_B)^{1/2}\right]$
Combination of film diffusion and ash diffusion controls	$t_t = t_f + t_A$ $t_t = \tau_f X_B + \tau_A[(1-X_B)\ln(1-X_B)+X_B]$
Combination of film diffusion and reaction controls	$t_t = t_f + t_r$ $t_t = \tau_f X_B + \tau_r\left[1-(1-X_B)^{1/2}\right]$
Combination of ash diffusion and reaction controls	$t_t = t_A + t_r$ $t_t = \tau_A[(1-X_B)\ln(1-X_B)+X_B] + \tau_r\left[1-(1-X_B)^{1/2}\right]$

Figure 4. Conversion versus residence time for plug flow when the chemical reaction rate is controlled by each of the resistances individually

Table 2. Conversion-time expressions for plug flow and the combination of resistances

Figure 3. Conversion versus time of Anthraqulnone reaction with the radius of 26.5µm [10]

	Reaction controls	Ash diffusion controls	Film diffusion controls
Plug Flow	$X_B = \dfrac{t}{\tau}$ $\tau_f = \dfrac{\rho_B R}{2\,bK_g C_{Ag}}$	$\dfrac{t}{\tau_A} = (1-X_B)\ln(1-X_B)+X_B$ $\tau_A = \dfrac{\rho_B R^2}{4\,bD_e C_{Ag}}$	$X_B = 1-\left(1-\dfrac{t}{\tau}\right)^2$ $\tau_r = \dfrac{\rho_B R}{bk''C_{Ag}}$
Mixed Flow	$\overline{X_B} = 1-\dfrac{\tau-\bar{t}}{\tau} -\dfrac{\bar{t}}{\tau}e^{-\frac{\tau}{\bar{t}}}$ $\tau_f = \dfrac{\rho_B R}{2\,bK_g C_{Ag}}$	$\overline{X_B} = 1-\displaystyle\int_0^\tau (1-X_B)\dfrac{e^{-\frac{t}{\bar{t}}}}{\bar{t}}dt$ $\dfrac{t}{\tau_A} = (1-X_B)\ln(1-X_B)+X_B$ $\tau_A = \dfrac{\rho_B R^2}{4\,bD_e C_{Ag}}$	$\overline{X_B} = 1-\dfrac{\tau^2-2\tau\bar{t}+2\bar{t}^2}{\tau^2} +\dfrac{2\bar{t}^2}{\tau^2}e^{-\frac{\tau}{\bar{t}}}$ $\tau_r = \dfrac{\rho_B R}{bk''C_{Ag}}$

In this case, the rate of chemical reaction is controlled by each of the resistances (including the gas film layer resistance, the ash layer resistance, and the chemical reaction resistance), individually. As can be seen in this figure, for a specified time, in the case the chemical reaction rate is controlled by the ash layer resistance, the conversion is greater than the rates of chemical reaction controlled by the other two regimes.

It has been assumed up to now that a single resistance controls throughout reaction of the cylindrical particle. However, the relative importance of the gas film, ash layer, and reaction steps will vary as particle conversion progresses. In the following, the effect of the combination of resistances on the conversion of reaction and the residence time of reaction is checked.
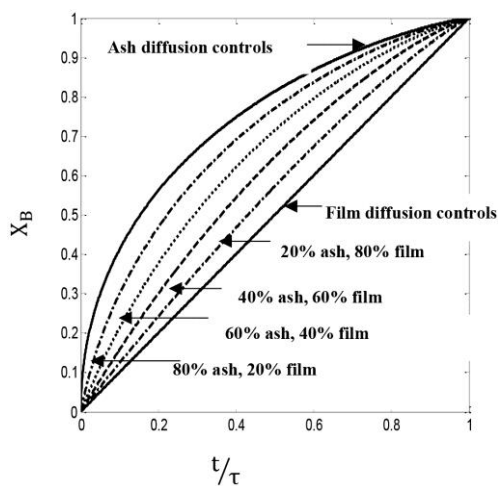
The effect of the combination of resistances including gas film layer resistance and ash layer resistance for a plug flow in the reactor filled with cylindrical particles has been studied. The results of this study are shown in Fig. (5).

In this case, gas film layer resistance and ash layer resistance control the rate of the reaction, simultaneously. According to this figure, for a specific conversion, by reducing gas film layer resistance and by increasing the ash layer resistance, the reaction time is reduced. It can also be said that for a specified time, by reducing gas film layer resistance and by increasing the ash layer resistance, the reaction conversion increases. When a hard solid ash forms during the reaction, the resistance of gas-phase reactant through this ash layer is usually much greater than that through the gas film surrounding the particle. Hence, in the presence of a nonflaking ash layer, film resistance can be safely ignored.
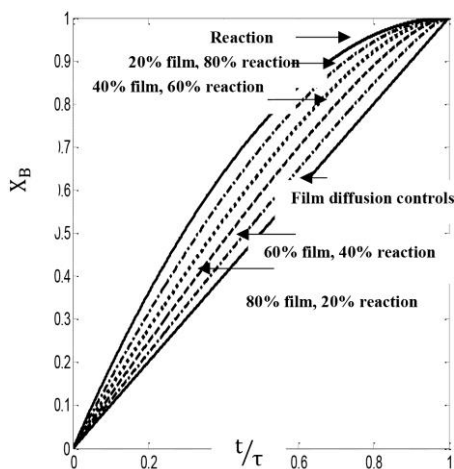
Fig. (6) shows the effect of the combination of resistances including gas film layer resistance and the chemical reaction resistance for a plug flow in the reactor filled with cylindrical particles. In this case, the gas film layer resistance and the chemical reaction resistance control the rate of the reaction, simultaneously.

The same situation can be seen in this figure. As can be seen, for a specific conversion, by reducing the gas film layer resistance and by increasing the chemical reaction resistance, the reaction time is reduced. Furthermore, for a specified time, by reducing the gas film layer resistance and by in-

creasing the chemical reaction resistance, the reaction conversion increases.

Figure 5. Conversion versus residence time for plug flow when the chemical reaction rate is controlled by the gas film layer resistance and the ash layer resistance simultaneously
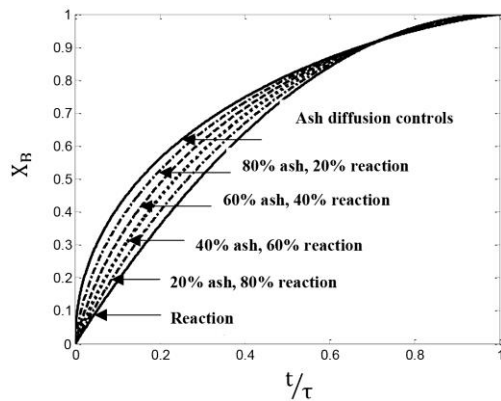

Figure 6. Conversion versus residence time for plug flow when the chemical reaction rate is controlled by the gas film layer resistance and the chemical reaction resistance simultaneously

The effect of the combination of resistances including the ash layer resistance and chemical reaction resistance for a plug flow in the reactor filled with cylindrical particles is illustrated in Fig. (7).

In this case, the ash layer resistance and chemical reaction resistance control the rate of the reaction, simultaneously.

As can be seen, for a specific conversion and for the conversions lower than 0.92, by increasing the ash layer resistance and by reducing the reaction resistance, the reaction time is reduced. For the conversions greater than 0.92, this trend is reversed. Moreover, for a specified time, by increasing the ash layer resistance and by reducing the chemical reaction resistance, the reaction conversion increases.

Figure 7. Conversion versus residence time for plug flow when the chemical reaction rate is controlled by the ash layer resistance and the chemical reaction resistance simultaneously
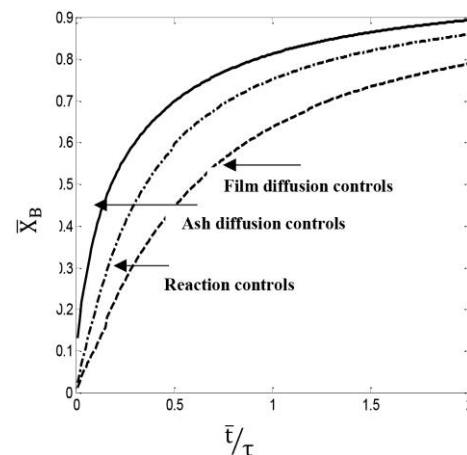
Fig. (8) shows the effect of three different resistance regimes for a plug flow in the reactor filled with cylindrical particles. In this case, the gas film layer resistance, the ash layer resistance, and the chemical reaction control the rate of the reaction, simultaneously. As can be observed in this figure, when the gas film layer resistance is considered to be fixed, for a specific conversion and for the conversions lower than 0.92, by increasing the ash layer resistance and by reducing the chemical reaction resistance, the reaction time is reduced. For the conversions greater than 0.92, this trend is reversed. Also, for a specified time, by increasing the ash layer resistance and by reducing the chemical reaction resistance, the reaction conversion increases.

Until now, the studies have been based on plug flow of cylindrical particles. But, from now on, in the following, the mixed flow of cylindrical particles is offered. The result of conversion versus time for a mixed flow in the reactor filled with cylindrical particles is given in Fig. (9).
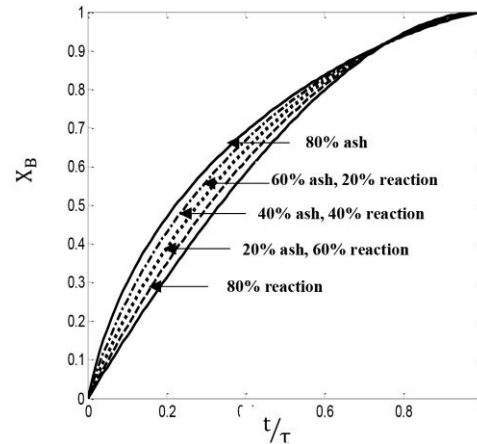
Figure 8. Conversion versus residence time for plug flow when the chemical reaction rate is controlled by the gas film layer resistance, the ash layer resistance, and chemical reaction resistance simultaneously

In this situation, the rate of chemical reaction is controlled by each of the resistances (including the gas film layer resistance, the ash layer resistance, and the chemical reaction resistance), individually. As can be seen in this figure, for a specified time, in the case the chemical reactions rate is controlled by the ash layer resistance, the conversion is greater than the rates of chemical reactions controlled by the other two regimes. On the other hand, for a specified reaction conversion, in the case of chemical reactions controlled by ash layer resistance, the time required for the rate of chemical reactions is less than that in the other two regimes.
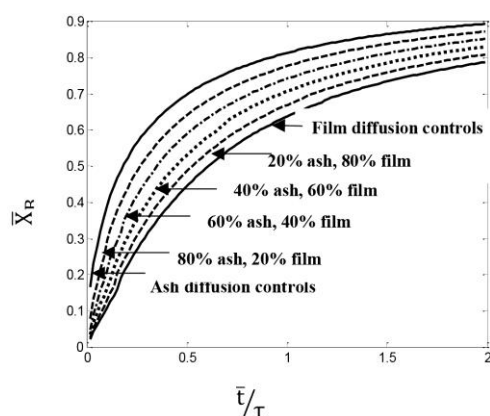

Figure 9. Conversion versus residence time for mixed flow when the chemical reaction rate is controlled by each of the resistances individually

The effect of the combination of resistances including the gas film layer resistance and ash layer resistance for a mixed flow in the reactor filled with cylindrical particles is illustrated in Fig. (10).

In this case, gas film layer resistance and ash layer resistance control the rate of the reaction, simultaneously. According to this figure, for a specific conversion, by reducing gas film layer resistance and by increasing the ash layer resistance, the reaction time is reduced. In other words, for a specified time, by reducing gas film layer resistance and by increasing the ash layer resistance, the reaction conversion increases.
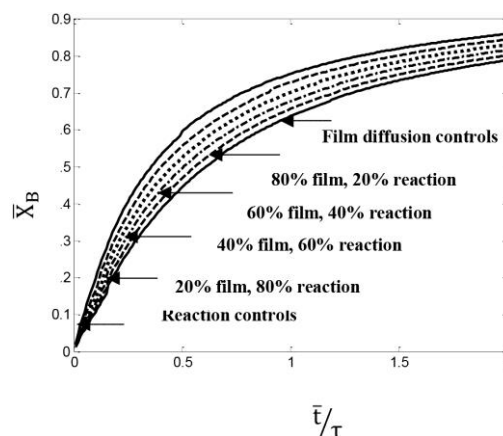

Figure 10. Conversion versus residence time for mixed flow when the chemical reaction rate is controlled by the gas film layer resistance and the ash layer resistance simultaneously

The result of conversion versus time for a mixed flow in the reactor filled with cylindrical particles is shown as in Fig. (11). In this case, the gas film layer resistance and the chemical reaction resistance control the rate of the reaction, simultaneously.

The same situation can be seen in this figure. As can be seen, for a specific conversion, by reducing the gas film layer resistance and by increasing the chemical reaction resistance, the reaction time is reduced. Furthermore, for a specified time, by reducing the gas film layer resistance and by increasing the chemical reaction resistance, the reaction conversion increases.

The effect of the combination of resistances including the ash layer resistance and chemical reaction resistance for a mixed flow in the reactor filled with cylindrical particles is illustrated in Fig. (12). In this situation, the ash layer resistance

and chemical reaction resistance control the rate of the reaction, simultaneously. As can be observed in this figure, by increasing the ash layer resistance and by reducing the reaction resistance, the reaction time is reduced. Moreover, for a specified time, by increasing the ash layer resistance and by reducing the chemical reaction resistance, the reaction conversion increases.
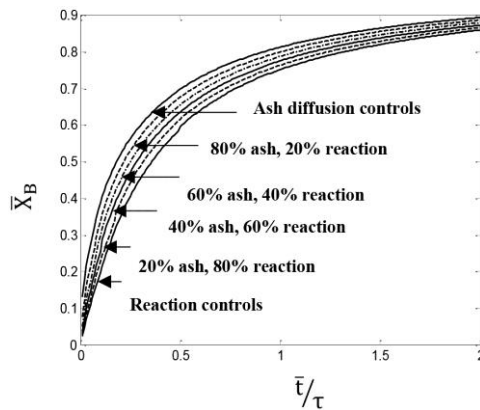

Figure 11. Conversion versus residence time for mixed flow when the chemical reaction rate is controlled by the gas film layer resistance and the chemical reaction resistance simultaneously

Finally, the effect of three different resistance regimes on the conversion of reaction and residence time for a mixed flow in the reactor filled with cylindrical particles is given in Fig. (13). In this case, the gas film layer resistance, the ash layer resistance, and the chemical reaction control the rate of the reaction, simultaneously. As can be seen in this figure, when the gas film layer resistance is considered to be fixed, for a specific conversion, by increasing the ash layer resistance and by reducing the chemical reaction resistance, the reaction time is reduced. Also, for a specified time, by increasing the ash layer resistance and by reducing the chemical reaction resistance, the reaction conversion increases.
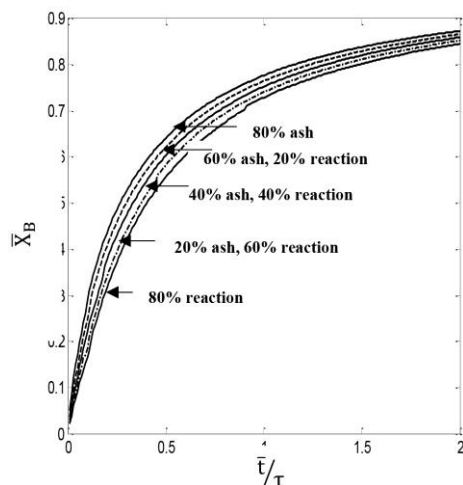
4. Conclusion

In this paper, a mathematical model was developed for calculating the conversion and residence time of the reaction for both plug flow and mixed flow in the reactors filled with cylindrical particles using the shrinking core model. The model

was developed for the case the chemical reaction rate was controlled by the gas film layer resistance, the ash layer resistance, and the chemical reaction resistance as well as the combination of them. The mentioned studies were related to innovations of this research. For evaluation of modeling, the results of the model were compared with experimental data. The results indicated that there was consistency between them. Also, The results showed at a certain time, when the rate of chemical reaction was controlled by each of the resistances individually, if the reaction was controlled by the ash layer resistance, then, the conversion rate was higher than that when the chemical reaction was controlled by the other two resistance regimes.

In addition, the results showed either resistance alone or a combination of them was effective on the conversion and residence time reaction. However, the relative importance of the gas film, ash layer, and chemical reaction steps would vary as particle conversion progressed. For a constant-size particle, the gas film resistance remained unchanged; the resistance to reaction increased as the surface of unreacted core decreased; and the ash layer resistance was nonexistent at the start because no ash was present, but became progressively important as the ash layer built up. In general, therefore, it may not be reasonable to consider that just one step controls throughout the reaction.

Figure 12. Conversion versus residence time for mixed flow when the chemical reaction rate is controlled by the chemical reaction resistance and the ash layer resistance simultaneously

Acknowledgements

Nomenclature

b	Stoichiometry coefficient of the component B
C_{Ag}	Concentration of A in the gas phase (mole/m³)
C_{As}	Concentration of A on the unreacted core surface (mole/m³)
E	The exit age distribution of the solids in the reactor
F	Total mole of feed
$F(R_i)$	Mole of feed with size R_i
L	Length of particle (m)
k_g	Mass transfer coefficient between fluid and particle
Mw	Molecular weight (g/gmole)
n_B	Number of moles of the reagent solid into the particle (mole)
N_B	Number of moles of solid (mole)
ρ_B	Molar density of B in the solid (mole/m³)
x_B	Solid conversion
$\overline{X}_B$	Mean solid conversion
R	Radius of particle (m)
r	Radius of particle (m)
r_c	Radius of the unreacted core, (m)
R_m	The largest particle size in the feed (m)
$R(t_p = \tau)$	Radius of the largest particle completely converted in the reactor
S_{ex}	External surface of particle (m²)
S_B	Surface of particle (m²)
t	Time of reaction (s)
τ	The time for complete conversion of a particle (S)
$\overline{t}$	Residence time (s)
V_B	Volume of particle (m³)

Figure 13. Conversion versus residence time for mixed flow when the chemical reaction rate is controlled by the gas film layer resistance, the ash layer resistance, and the chemical reaction resistance simultaneously

References

1. Levenspiel, O. (1999). "Chemical Reaction Engineering." Third Edition, John Wiley & Sons, New York.

2. Gbor, P. K., Jia, C. Q. (2004). "Critical evaluation of coupling particle size distribution with the shrinking core model." *Chemical Engineering Science*, Vol. 59, pp. 1979-1987.

3. Noorman, S., Gallucci, F., Annaland, V.S.M., Kuipers, J.A.M. (2011). "A theoretical investigation of CLC in packed beds. Part 1: Particle model." *Chemical EngineeringJournal*, Vol. 167, pp. 297-307.

4. Tsinontides, S. C., Jackson, R. (1993). "The mechanics of gas fluidized beds with an interval of stable fluidization." *Journal Fluid Mechanic*, Vol. 255, pp. 231-214.

5. Fan, L.S. (1989). "Gas-Liquid-Solid Fluidization Engineering." Butterworths, Stoneham, MA, 1989.

6. Ebrahimi, A.A., Ebrahim, H.A., Jamshidi, E. (2008). "Solving partial differential equations of gas–solid reactions by orthogonal collocation." *Computers and Chemical Engineering*, Vol. 32, pp.1746–1759.

7. Movagarnejad, K., Sohrabi, M., Kaghazchi, T., Vahabzadeh,F. (2000). ''A model for the rate of enzymatic hydrolysis of cellulose in heterogeneous solid–liquid systems.'' *Biochemical Engineering Journal*, Vol. 4, pp. 197–206.

8. Yagi, S., Kunii, D. (1995). "Studies on combustion of carbon particles in flames and fluidized beds." *The 5th Symposium on Combustion*, New York, USA, pp. 231-236.

9. Sleekly, J., Evans, J.W., Sohn, H.Y. (1976). "Gas-solid reactions." Academic Press.

10. Schmidt, L. D. (1998). "The Engineering of Chemical Reactions." New York: Oxford University Press.

11. Abad, A., Adanez, J., Cuadrat, A., Garcia-Labiano, F., Gayan, P., de Diego, L.F. (2011). "Kinetics of redox reactions of ilmenite for chemical-looping combustion." *Chemical Engineering Science*, Vol. 66, pp. 689-702.

12. Amiri, A., Ingram, G.D., Bekker, A.V., Livk, I., Maynard, N.E. (2013). "A multi-stage, multi-reaction shrinking core model for self-inhibiting gas-solid reactions." *Adv. Powder Technol.*, Vol. 24, pp. 728-736.

13. Gbor, P. K., Jia, C.Q. (2004). "Critical evaluation of coupling particle size distribution with the shrinking core model." *Chemical Engineering Science*, Vol. 59, pp. 1979-1987.

14. Kruggel-Emden, H., Rickelt, S., Stepanek, F. (2010). "Development and testing of an interconnected multiphase CFD-model for chemical looping combustion." *Chemical Engineering Science*, Vol. 65, pp. 4732-4745.

15. Kruggel-Emden, H., Stepanek, F. (2011). "A study on the role of reaction modeling in Multi-phase CFD-based simulations of Chemical Looping Combustion." *Oil and Gas Science and Technology*, Vol. 66, pp. 313-331.

16. Parisi, D.R., Laborde, M.A. (2004). "Modeling of counter-current moving bed gas-solid reactor used in thedirect reduction of iron ore." *Chemical Engineering Journal*, Vol. 104, pp. 35-43.

17. Rodriguez F., Revenga J., Tijero J. (1996). ''Study of anthraquinone reaction with sodium sulfide.'' *The Chemical Engineering Journal and the Biochemical Engineering Journal*, Vol. 63, pp. 37-43.