Fuel 129 (2014) 231–237

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

A novel dimensionless form of unreacted shrinking core model for solid conversion during chemical looping combustion

Xunliang Liu *, Fuqiang Song, Zhi Wen

School of Mechanical Engineering, University of Science and Technology Beijing, Beijing 100083, China

HIGHLIGHTS

- A novel dimensionless integral form of USCM is derived from the original one.
- Four dimensionless groups are used to correlate solid conversion with other parameters.
- Influences of dimensionless groups on solid conversion are investigated.
- The dimensionless velocity of reaction front is obtained to characterize CL processes.

ARTICLE INFO

Article history:
Received 13 December 2013
Received in revised form 19 March 2014
Accepted 3 April 2014
Available online 18 April 2014

Keywords:
Chemical looping
Solid conversion
Unreacted shrinking core model
Dimensionless form

ABSTRACT

In this paper, a novel dimensionless integral form of the unreacted shrinking core model (USCM) was derived from its original one to describe the redox reaction of oxygen carrier (OC) particles during chemical looping (CL) processes. Four dimensionless groups of the relevant parameters were introduced to correlate solid conversion with other parameters. The analysis revealed that three dimensionless groups are important for characterizing solid conversion, including Fo′, Bi′ and Rc. The group Bi′ has less effect on the solid conversion if Bi′ is larger than 10. The intrinsic reaction rate exerts a significant influence on the conversion when Rc is less than 10. The conversion rate is more sensitive to Rc while Rc is less than 1.The reaction front σ is related to the above three dimensionless groups of parameters as well. The dimensionless velocity of reaction front (dσ/d Fo′) is obtained to characterize the CL processes.

1. Introduction

Recently, the chemical looping (CL) process has been comprehensively investigated as a new approach for CO_2 capture or gasification, which has outstanding advantages over the traditional technologies. Most of the research and development work on the CL processes has been focused on the design and synthesis of oxygen carrier (OC), fixed- or fluidized-bed reactor design and operation, and theoretical analysis and demonstration of the looping process.

Kinetic studies on the reaction mechanism of CL processes are important for reactor design and performance. As reviewed by Hossain [1], two general types of models have been developed to represent the kinetics of reduction and oxidation of OC particles during CL processes: (i) the nucleation and nuclei growth model [2–4] and (ii) the unreacted shrinking core model (USCM) [5–19]. In particular, the merit of the USCM is that it takes into account the variation of the gas concentration and reactor temperature during operation of the CL system [8,9].

The USCM incorporates the dependence of particle size and pore structure of the solid reactant particles on the rate of reaction. According to this model, as the reaction progresses the metal–metal oxide interface moves towards the center of the grain, leaving behind a porous metallic/metal oxide product layer through which gaseous reactants and products diffuse [10,11]. The surface (front) separates the solid reactant core from the outer ash (product) layer, as illustrated in Fig. 1. Initially, the external surface of the solid takes part in the reaction. The thickness of the ash layer increases with time leading to the shrinking core of unreacted solid. Therefore, the heterogeneous reaction proceeds via three steps: (i) external mass transfer, (ii) internal mass transfer, and (iii) chemical reaction.

Ishida and Jin [12] first tested this model on NiO/YSZ particles considering all of the above three steps. They found that the reduction reaction rate was mainly controlled by the strongly temperature-dependent intrinsic reaction step, and the oxidation reaction rate was controlled by both the chemical reaction and the

* Corresponding author. Tel.: +86 10 62332730; fax: +86 10 62332741.
E-mail address: liuxl@me.ustb.edu.cn (X. Liu).

http://dx.doi.org/10.1016/j.fuel.2014.04.006
0016-2361/

Nomenclature

C_A	concentration of species A (mol/m^3)
C_{co}	concentration of CO (mol/m^3)
d_p	diameter of OC particles (m)
D_A	mass diffusivity of species A (m^2/s)
D_{co}	mass diffusivity of CO (m^2/s)
D_e	effective mass diffusivity (m^2/s)
D_{Kn}	Knudsen diffusivity (m^2/s)
D_{pore}	mass diffusivity inside mesopores (m^2/s)
E_a	activation energy (kJ/mol)
h_m	external mass-transfer coefficient (m/s)
k	reaction rate constant (m^{3n-2}/(mol^{n-1} s))
k_0	pre-exponential factor (m^{3n-2}/(mol^{n-1} s))
k_V	intrinsic volumetric reaction rate constant (1/s)
n	reaction order
r_c	radius of unreacted core or reaction front (m)
R	radius of OC particles (m); universal gas constant, 8.314 J/(mol K)
Re	Reynolds number
Rc	reaction constant number
Sc	Schmidt number
Sh	Sherwood number
t	time (s)
T	reacting temperature (K)
U	gas velocity (m/s)
X	solid conversion

Greek letters

$\rho_{B,\,m}$	molar density of solid material B (mol/m^3)
ν	stoichiometric coefficient
σ	dimensionless position of reaction front
ϕ	Thiele modulus
υ	kinetic viscosity of gas (m^2/s)
ε	porosity
τ	tortuosity

ash-layer diffusion. Similar results were reported by Ryu et al. [13] using an integral form of the USCM with the external mass transfer neglected. Garcia-Labiano et al. [14,15] studied the reaction kinetics, considering the structural variations of the oxygen carrier. While preparing for the oxygen carrier, small particles (30–70 μm) were selected to minimize mass transfer limitations. Plate and spherical geometries were studied using the changing-grain-size model based on the reaction-controlled mechanism. Similar approaches for studying reaction kinetics of OC particles or simulating the performance of a CL reactor were adopted in some research literatures [16–19].

In this paper, a novel dimensionless integral form of the USCM is derived from its original one to describe the redox reaction of OC particles during CL processes. Four dimensionless groups of the relevant parameters are introduced to depict the relation of the three steps of reaction kinetics. The effects of key parameters on the conversion level of OC particles are analyzed with the new integral form. The dimensionless velocity of the reaction front is obtained to characterize the CL processes.

2. The novel dimensionless integral form of the USCM

For OC particles involved in the CL process, the USCM is based on the following assumptions: (i) the particle is spherical and its volume is constant; (ii) mass and density changes of the particle are expected to vary only slightly; (iii) the particle is isothermal and the structure of the porous particle is uniform, which can be represented by a porosity, a tortuosity and an average pore size.

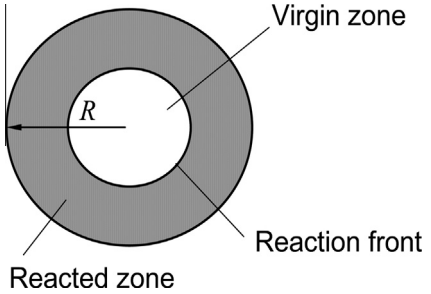

Fig. 1. Sketch of the unreacted shrinking core model.

(iv) It is assumed that the porosity of the unreacted core is very small, so that the unreacted solid material is practically impervious to the reactant gases.

2.1. Derivation of the novel integral form of the UCM

The USCM is refined below to describe the redox reaction of the OC particle. The redox reaction is assumed as a hypothetical gas–solid reaction [11]:

$$A(g) + bB(s) \rightarrow cC(g) + dD(s) \tag{1}$$

According to the USCM, the change of the core radius (r_c) can be expressed as

$$\frac{dr_c}{dt} = -\frac{\nu C_A}{\rho_{B,m}} \Big/ \left[\frac{r_c^2}{R^2 h_m} + \frac{(R-r_c)r_c}{RD_e} + \frac{1}{kC_A^{n-1}}\right] \tag{2}$$

where ν is the stoichiometric coefficient, C_A is the molar concentration of the gas species A, $\rho_{B,m}$ indicates the molar density of the solid, R is the radius (m) of the OC particle, h_m represents the gas film mass-transfer coefficient, D_e is the effective diffusivity of gas species A through the ash layer, k represents the reaction rate constant, and n is the reaction order.

The three terms in the denominator of Eq. (2) represent the external gas film diffusion, the ash-layer diffusion and the chemical reaction rate, respectively.

Eq. (2) can be transformed into

$$\frac{\nu C_A}{\rho_{B,m}} dt = -\left[\frac{r_c^2}{R^2 h_m} + \frac{(R-r_c)r_c}{RD_e} + \frac{1}{kC_A^{n-1}}\right] dr_c \tag{3}$$

After integration, we obtained the integral form of the USCM as follows.

$$\frac{\nu C_A}{\rho_{B,m}} t = \left[\frac{R}{3h_m} + \frac{R^2}{6D_e} + \frac{R}{KC_A^{n-1}}\right] - \left[\frac{r_c^3}{3R^2 h_m} + \frac{(3Rr_c^2 - 2r_c^3)}{6RD_e} + \frac{r_c}{KC_A^{n-1}}\right] \tag{4}$$