

ALTERNATIVE CONTROL OF NANOPARTICLES DISPERSITY IN HIGH-TEMPERATURE FLOW REACTORS

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ABSTRACT: *The 1-dimensional model of aerosol process which includes a hot aerosol stream flowing through a tube with thermal gradients between the aerosol stream and the reactor cooled walls was developed to predict the aerosol formation, growth and thermophoretic deposition in high-temperature reactors. The mass and energy conservation equations were solved to determine the concentration and temperature profiles of the components. The model includes particle formation by nucleation, growth by coagulation, Brownian diffusion as well as the loss of aerosol particles by thermophoretic deposition on the cold reactor walls. The developed model results in the system of ordinary differential equations which were solved in SCILAB software.*

Keywords: *Thermophoretic deposition, Coagulation, Nucleation, Modeling*

INTRODUCTION

Nanoparticles are at the core of nanotechnology. These are particles ranging in size from 1 millionth to 100 millionths part of a millimeter, more than 1,000 times smaller than the diameter of a hair. In this order of magnitude, it is not only the chemical composition but also the size and the shape of the particles that determine their properties. Measurements in gas-phase reactors are quite problematic as time scales are extremely small, temperatures very high and the gaseous atmosphere is often aggressive. Therefore, process simulation is a useful tool and can significantly improve the general understanding of particle formation and moreover can support product and process optimization.

It is crucial to understand the behavior of fine particles in order to control them. Transport of fine particles from fluid stream to reactor surface is important in predicting the rate of wall deposition and in understanding mechanisms that lead to particle removal.

It is known that thermophoretic transport is one of the many methods which causes smaller particles to deposit on the nearest surfaces.

Thermophoresis is of practical importance in many engineering applications such as thermal precipitators, the distribution of soot in combustion systems and thermophoretic deposition of particulate matter onto walls of piping systems. It is the phenomenon where very small aerosol particles experience a net thermophoretic force when suspended in a gas in which a temperature gradient is present. This force results from an imbalance in momentum transfer associated with molecular collisions between the hot and cold sides of the particles. Therefore, this force tends to drive the particles in the direction of negative temperature gradient.

Thermophoresis has both negative and positive effects in application areas. Negative effects of thermophoresis include reduction of thermal conductivity of heat exchanger pipes and reduction of production yield of specialty powders manufactured in high temperature aerosol reactors. On the other hand, the concept of thermophoresis provides a working principle to fabricate optical fibre in a modified chemical vapor deposition (MCVD) process. It also can be employed to remove or sample atmospheric particles from the air in a thermal precipitator.

Nomenclature

A	Total particle area concentration (cm^2/cm^3)
c	Monomer Particle velocity, (m/s)
C	Cooling gradient, (K/m)
C_i	TiCl ₄ concentration (mol/cm^3)
C_c	Slip correction factor, dimensionless
D	Particle diffusivity, (m^2/s)
D_{se}	Diffusion coefficient, (cm^2/s)
d_p	Particle diameter, (m)
λ	Mean free path, (m)
I	Nucleation rate (# cm^3/s)
k	TiCl ₄ overall oxidation rate constant (1/s)
k_g	TiCl ₄ gas phase reaction rate constant (1/s)
k_s	TiCl ₄ surface reaction rate constant (cm/s)
k_B	Boltzman constant, ($\text{gcm}^2\text{s}^{-2}\text{K}^{-1}$)
$K_{g,l}$	Gas thermal Conductivity
Kn_g	Knudsen number of the gas
$K_{p,l}$	Particle thermal Conductivity
K_{th}	Thermophoretic coefficient
N_{Avo}	Avogadro's number (1/mol)
N	Particle number concentration (# $1/\text{cm}^3$)
PSD	Particle size distribution
R_i	Universal gas constant, ($\text{Kgm}^2\text{s}^{-2}\text{K}^{-1}\text{mol}^{-1}$)
R	Radius of reactor, (m)
T	Absolute Temperature, (K)
T_w	Wall temperature, (K)
T_{ref}	Reference temperature
U_{th}	Thermophoretic velocity, (m/s)
V	Particle volume concentration (# $1/\text{cm}^3$)
z	Axial direction, (m)
Greek letters	
β	Collision frequency for TiO ₂ particles (cm^3/s)
μ_g	Dynamic viscosity, (Pa.s)
ρ	Gas density, (g/cm^3)

Fundamental research in to this phenomena has been has been reviewed by a number of authors including Talbot, Cheng, Schefer, and Willis (1980), Bakanov (1995), Li and Davis (1995a,b), and Lee and Kim (2001). Typical characteristics of processes of thermophoresis include a hot aerosol stream flowing through a tube or an annulus, and the presence of a non-negligible thermal gradient between the aerosol stream and the cooled walls of the

tube or of an outer tube of the annulus. Accordingly, many thermophoresis studies have targeted these geometries.

Thermophoretic deposition of particles in an annular flow was studied theoretically by Weinberg (1983) and Fiebig, Hilgenstock, and Riemann (1988). Weinberg (1983) suggested that complete collection was possible with thermophoresis and that a smaller separation distance between concentric cylinders resulted in higher deposition efficiency. Fiebig et al. (1988) showed that when the annulus was oriented vertically, as a result of the buoyancy effect, the deposition efficiency tended to increase for a smaller ratio of inner to outer tube radius. Chang, Ranade, and Gentry (1992, 1995) carried out experiments and numerical simulations to quantify thermophoretic deposition in an annular flow system with fixed thermal gradients between two concentric cylinders. They found good agreement between experimental results and computational results using the model of Talbot et al. (1980). Lee and Kim (2001) studied thermophoretic deposition experimentally and numerically in an annular flow system using several models suggested by Derjaguin, Ravinovich, Storozhilova, and Shcherbina (1976) and Talbot et al. (1980) in a cryogenic temperature range. They found that the thermophoretic models required modification in the cryogenic temperature range. A tube flow with a thermal gradient has been utilized in many applications including heat exchanger pipes and automobile exhaust pipes.

Therefore, it is necessary to study thermophoresis in a tube flow in order to understand and innovate a number of systems that are employed in a variety of applications. The specific details of the problem we are treating are assumed to be as follows: the gas enters with an initial particle concentration and volume, with the maximum temperature of the fluid, and flows through the reactor with a wall temperature also equal to the fluid temperature at the reactor entrance. At some distance far enough downstream such that the laminar incompressible flow is fully developed, the wall temperature decreases to a minimum temperature and remains there. Convection, Brownian diffusion, and thermophoresis are the main mechanisms involved in such systems.

The goal of the analysis is to develop a 1-dimensional mathematical model of aerosol dynamics to gain insight into the details of particle growth and formation, as well as to investigate the effect of thermophoretic wall deposition of the particle size at the outlet of the reactor.

THEORETICAL APPROACH

Reaction model

The formation of TiO₂ takes place by the overall reaction of TiCl₄ with O₂:



The depletion of TiCl₄ occurs by both homogeneous gas phase reaction and by the reaction at the surface of existing TiO₂ particles:

$$\left(\frac{dC_i}{dt}\right) = -k \cdot C_i = -(k_g + k_s \cdot A)C_i \quad (2)$$

where C_i (mol/cm³) is the concentration of TiCl₄, t(s) is the residence time, A (cm²/cm³) is the surface area concentration of TiO₂ particles, k (1/s) is the overall oxidation rate constant of TiCl₄ (Pratsinis et al., 1999):

$$k_s = 4,9e + 03 \exp\left(-\frac{80993}{T}\right) \quad (3)$$

While k_g (1/s) is the gas phase reaction rate constant, T (K) is the process temperature and k_s (cm/s) is the surface reaction rate constant (Pratsinis, & Spicer, 1998):

$$k_s = 4,9e + 03 \exp\left(-\frac{80993}{T}\right) \quad (4)$$

Monodisperse Model

The computational scheme simulates homogeneous nucleation and coagulation/ coalescence as well as aerosol transport by diffusion and thermophoresis. Spherical

particles are assumed, $dp = \left(\frac{6V}{N\pi}\right)^{\frac{1}{3}}$ the overall process

is represented by the general dynamic equation for aerosol particles (e.g. Friedlander, 2000). For the differential particle number concentration $N=N(z, dp, t)$, where z denotes the direction, t time and dp particle diameter, the general dynamic equation can be written as:

$$\begin{aligned} \frac{dN}{dt} + \frac{1}{v} \frac{d}{dt} (U_{th} \cdot N) + \frac{1}{v} \frac{d}{dt} \left(-D_{SE} \cdot \frac{dN}{dt}\right) \\ = \left(\frac{dN}{dt}\right)_{NUCLE} + \left(\frac{dN}{dt}\right)_{COAG} \end{aligned} \quad (5)$$

Here U_{th} is the particle drift velocity due to thermophoresis, and D_{SE} is the particle diffusion coefficient. The left-hand side of the equation has terms that refer to temporal, convective and diffusive rates of change in the differential particle number concentration. The right-hand side has source terms for aerosol dynamics due to nucleation, and coagulation.

Brownian diffusion

The variation of particle number concentration with time can be determined by solving the one-dimensional equation of diffusion, given as follows:

$$\frac{dN}{dt} = D_{SE} \frac{d^2N}{dz^2} \text{ For axial direction} \quad (6)$$

The particle diffusion coefficient is given by the Stokes Einstein relation (e.g. Hinds, 1999):

$$D_{SE} = \frac{kB \cdot T \cdot Cc}{3\pi \cdot \mu \cdot g \cdot dp} \quad (7)$$

$$Cc = 1 + Kn_g \left(1.257 + 0.4e^{\frac{-1.1}{Kn_g}}\right) \quad (8)$$

Thermophoretic velocity

The thermophoretic particle drift velocity is modeled with Talbot equation (Talbot *et al.*, 1980) and is given by:

$$U_{th} = \frac{-K_{th} \cdot \mu_g}{\rho} \left(\frac{\nabla T}{T}\right) \text{ with } \nabla T \text{ in radial direction} \quad (9)$$

The expression for temperature as a function of time is obtained by fitting the polynomial function with the calculated dimensionless temperature difference, from equation (10)

$$\theta = \sum_{n=3}^{\infty} C_n R_n \left(\frac{r}{R} \right) e(-\lambda_n^2) \cdot \left[\left(\frac{x}{R} \right) \cdot (\text{Re Pr})^{-1} \right] \quad (10)$$

In the above equation, the value of θ , C_n , λ_n , $R_n \left(\frac{r}{R} \right)$

and n are dimensionless temperature, the coefficient of the Graetz equation, the eigenvalues, eigenfunction, and the number of terms respectively.

$$\theta = \frac{T(r, z) - T_w}{T_g - T_w} \quad (11)$$

$$T(r, z) = \theta(T_g - T_w) + T_w \quad (11a)$$

According to Eq (11a), the temperature profile $T(z, r)$ can be calculated.

$$C_n = (-1)^n \cdot 2.84606 \cdot \lambda_n^{(-1/3)} \quad (12)$$

$$\text{The eigenvalues, } \lambda_n = 4n + \frac{8}{3} \quad (13)$$

$$n = 1, 2, 3, 4, \dots$$

The thermophoretic coefficient (K_{th}) for a spherical particle applicable for all flow regimes from free molecular to continuum regimes is given by:

$$K_{th} = 2.294 * Cc \frac{\left(\frac{k_{g1}}{k_{p1}} + 2.2Kn_g \right)}{\left(1 + 3.483 * Kn_g \left(1 + 2 \frac{k_{g1}}{k_{p1}} + 4.4Kn_g \right) \right)} \quad (14)$$

Nucleation kinetics

$$\left(\frac{dN}{dt} \right)_{NUCL} = I = k \cdot C_i \cdot N_{Avo} \quad (15)$$

The change of the number concentration N is proportional to the nucleation rate I . Nucleation rate depends on the rate of chemical reaction of $TiCl_4$ oxidation.

2.2.4 Coagulation

This coagulation process leads to substantial changes in particle size distribution with time. Simple defining equation for coagulation is given by equation (16)

$$\left(\frac{dN}{dt} \right)_{COAG} = -\frac{1}{2} \cdot \beta \cdot N^2 \quad (16)$$

where β is the collision frequency function of equally sized particles from free molecule to continuum particle size regime (Hidy, G.M. (1984)):

$$\beta = 8\pi D d_p \left[\frac{d_p}{d_p \sqrt{2g}} + \frac{4\sqrt{2D}}{c d_p} \right]^{-1} \quad (17)$$

with the particle diameter, velocity and diffusivity, d_p , c and D , respectively, while the parameters

$$g = \frac{1}{3d_p I_a} \left[(d_p + I_a)^3 - (d_p^2 + I_a^2)^{\frac{3}{2}} \right] - d_p \quad (18)$$

$$D = \frac{k_B T}{3\pi\mu_g \nu_p} \left[\frac{5 + 4K_n + 6K_n^2 + 18K_n^3}{5 - K_n + (8 + \pi)K_n^2} \right] \quad (19)$$

with the mean free path for the particles

$$I_a = \frac{8D}{\pi c} \quad (20)$$

and

$$c = \sqrt{\frac{8k_B T}{\pi\rho_p \nu_p}} \quad (21)$$

The temperature along the reactor axis is a function of distance.

$$T = f(z), \quad (22)$$

where $T = f(z)$ is a function approximating the axial temperature distribution in the reactor. The temperature dependant terms are recalculated for the variable cooling gradient, C ; the temperature is given as

Table 1: Simulation conditions

Typical simulation parameters	Values
T (K)	1000
P (Pa)	1.013 e+5
R_i	8.314
N_{Avo} (1/mol)	6.02E+23
ρ_p (kg/m ³)	4200
ρ_s (kg/m ³)	$P \cdot M_{w_gas} / (R \cdot T)$
kB	$R_i / 6.022e+23$
$m(TiO_2)$ (kg)	1.33E-25
$v(TiO_2)$ (m ³)	3.16E-29
$s(TiO_2)$ (m ²)	1.16E-19
$d(TiO_2)$ (m)	3.93E-10
Q_n (m ³ /s)	$2 / (1000 \cdot 60)$
T_{rt} (K)	273
Q (m ³ /s)	$Q_{rt} \cdot T / T_{rt}$
$d_g(O_2)$ (m)	7.98E-09

$$T = T_0 - C \cdot z \quad (23)$$

Equations (1) – (23) are solved simultaneously using the software SCILAB.

RESULTS AND DISCUSSION

The change of temperature within the reactor is shown in Fig.1 (A). It can be seen that the temperature at the reactor entrance is high, and lower as it approaches the reactor exit. The change in temperature is caused by the heat transfer between the hot fluid and the cold reactor wall. Fig.1 (B) shows how the concentration of precursor varies with the temperature. The change in the initial temperature value will affect the radial temperature gradient inside the reactor. Increasing the initial temperature value will result in more of $TiCl_4$ converted, and lead to the increase in the rate of nucleation and thus decrease the particle number concentration and also lower the particle size whereas the particle surface area increases.

The degree of thermophoretic deposition depends directly on the level of cooling applied. Thermophoretic effect was tested by changing the cooling gradient in the axial direction of the reactor by calculating the radial temperature gradient while maintaining the initial temperature value constant. When the radial temperature gradient is greater than the axial temperature gradient, particles are moved to the wall due to higher radial gradient in comparison with axial gradient. The axial temperature distribution is expressed by Eq(23). The axial temperature gradient is expressed by coefficient C in Eq(23). When axial temperature changes, automatically the radial temperature gradient changes through Eq (11), which represents dimensionless temperature difference between axial temperature and wall temperature. Fig.1 - Fig.3 show the particle behavior along the reactor axis with varying axial cooling gradient, 700, 1000, and 1200 K/m, respectively. Fig.1 (C&D) shows that the particle number concentration at the reactor entrance is very low and becomes high downstream, which later decreases near the reactor wall. This explains that particle number concentration initially rises due to chemical reaction and when the raw material ($TiCl_4$) is depleted, coagulation causes particle number concentration to decrease.

In Fig.1 (D), the run without thermophoresis showed that Brownian diffusion is dominant. The deposition rate due to thermophoresis decreases with increase in time. This can be due to the decrease in the magnitude of thermophoresis as the particle increase. Particle losses to the wall become much higher when the cooling gradient of the aerosol flow is decreased. As Fig.2 (C) and Fig.3 indicate, when the cooling gradient of the aerosol flow is decreased, the loss of ultrafine particles becomes higher due to an increase in the thermophoretic velocity which causes the particles to move faster and deposit on the wall of the reactor. Fig.2 (B) shows the effect of temperature on thermophoretic velocity. Thermophoretic velocity is directly proportional to the inverse of absolute temperature, i.e. when the temperature increases, the negative thermal gradient increases, and so the increase in thermophoretic velocity is favored.

Fig.2 (A) shows how the system is affected at lower cooling gradients. We see that the average primary diameter of TiO_2 particles is reduced as the cooling gradient falls.

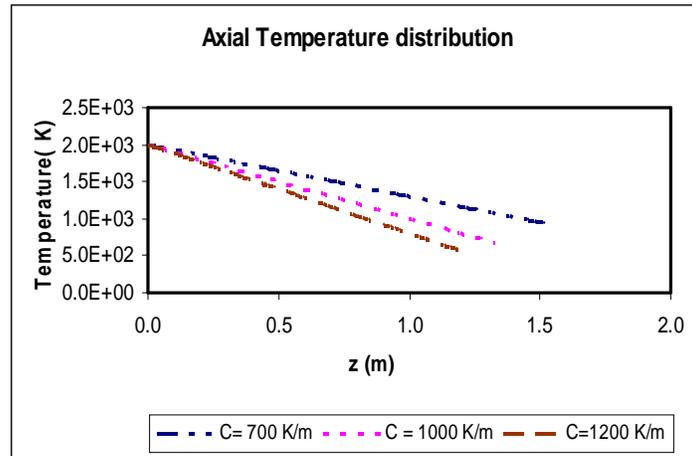


Figure 1(A): Temperature profile inside the reactor through the variation of cooling gradients.

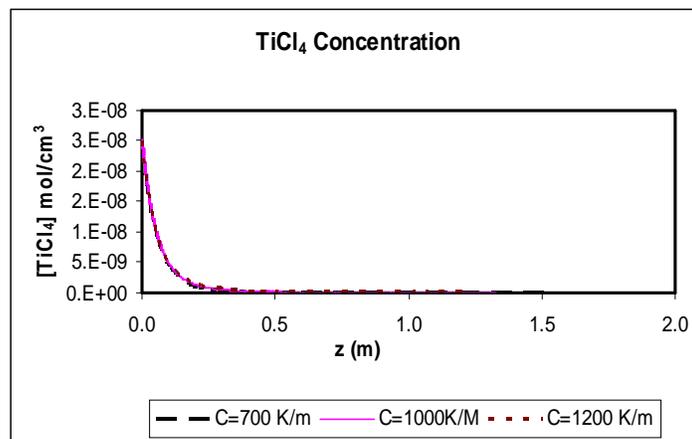


Figure 1(B): Increasing the initial temperature value will result in more of TiCl₄ converted, and lead to the increase in the rate of nucleation with no effect of temperature gradient on the conversion of titanium chloride to form titania.

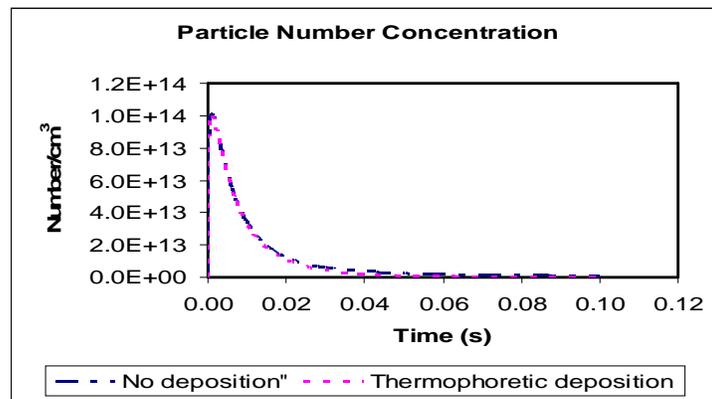


Figure 1 (C): The comparison between the particle number concentration with and without thermophoretic deposition

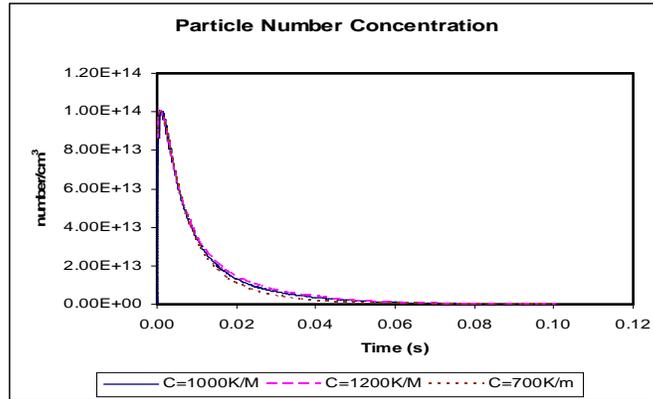


Figure 1(D): The effect of particle diameter on particle number concentration by varying the cooling gradients. Particle number concentration initially rises due to chemical reaction and later decreases when coagulation takes over

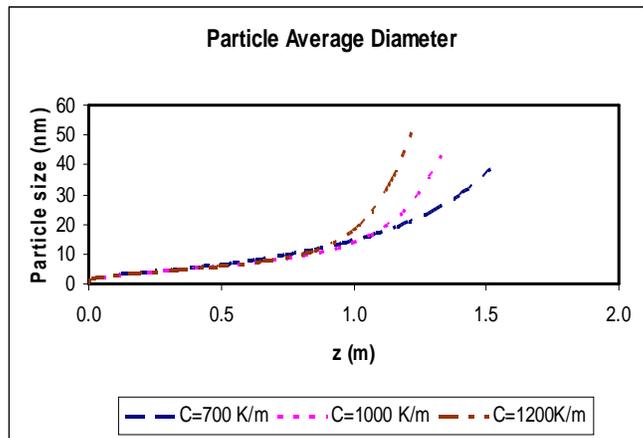


Figure 2 (A): The effect of axial distance on particle size by varying the cooling gradients. The large sized particles are observed on the lesser axial distance with a large cooling gradient

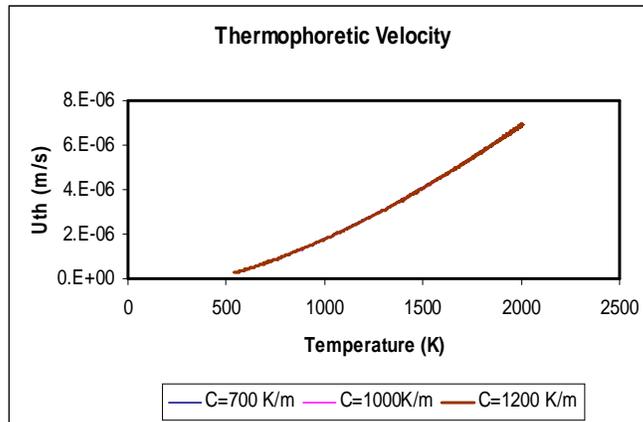


Figure 2 (B): The effect of temperature on thermophoretic velocity with the variation of cooling gradient

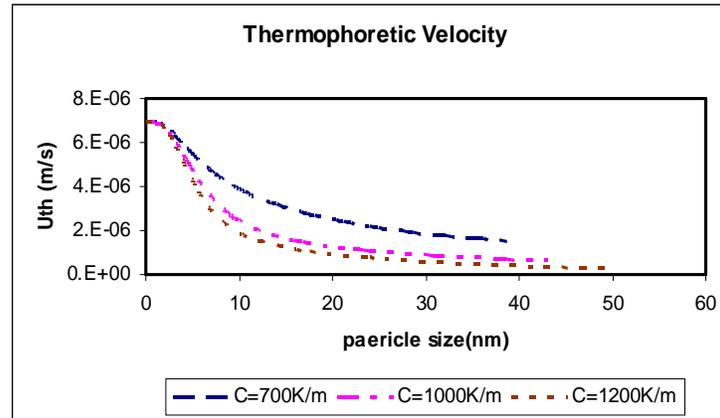


Figure 2 (C): The effect of particle size on deposition velocity, when the initial temperature value is kept constant at varying cooling gradients

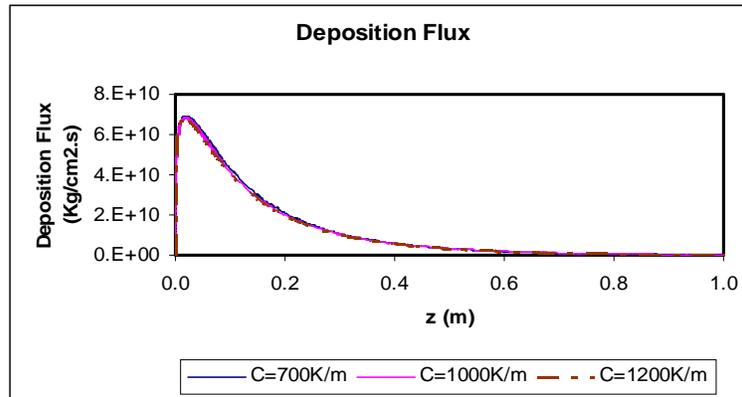


Figure 3(A): Effect of particle size on the deposition flux.

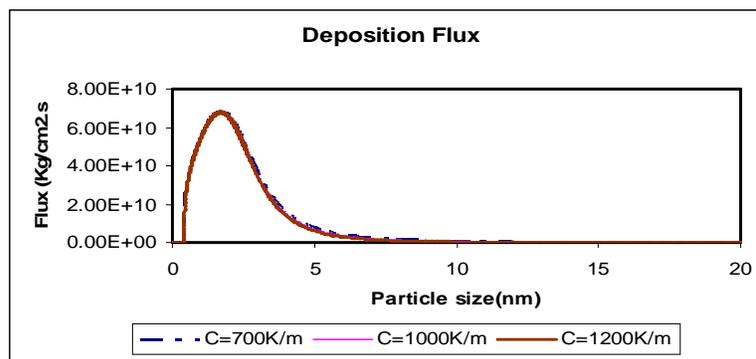


Figure 3(B): Effect of axial distance on the deposition flux

The effect of particle size on deposition velocity, when the initial temperature value is kept constant and varying the cooling gradient, is depicted in Fig.2 (C). Thermophoretic velocity decreases as the particle size increases.

With the assumption made, it can be seen from the graphs that thermophoretic force does not play some major role in the deposition of fine particles to the wall. However, the real high temperature reactors will also operate in turbulent mode and therefore particle wall deposition due to turbulent flows near the wall will play a role in the process.

CONCLUSION

The simulations were run using the conditions in Table 1. The simulation results obtained from the one-dimensional model provides useful information of the temperature and cooling gradient effects on the average titania particle diameter, particle concentration and thermophoretic velocity of particles at reasonable computational time. The effect of cooling gradient on thermophoretic velocity was clearly studied, ranging from 700 to 1200 K/m.

Based on the final results, the following conclusions have been made:

1. Thermophoretic velocity increases with increase in the cooling gradient and the distance of deposition, but decreases with increase in particle size.
2. Thermophoretic velocity affects the deposition flux and particle number concentration directly. From the results given, we have seen that particle number concentration and deposition flux does not change with particle size when varying the cooling gradient. This results when the increase in the cooling gradient causes the absolute temperature to increase simultaneously and offset the process. This shows that the thermophoretic velocity, deposition flux, particle number concentration and average particle size are implicit functions of temperature.
3. The effect of temperature on thermophoretic velocity is independent of the cooling gradient. Thermophoretic velocity increases with increase in temperature regardless of variation of the cooling gradient.

4. Thermophoretic velocity is directly proportional to the inverse of absolute temperature, i.e. when the temperature increases, the negative thermal gradient also increases, and so with thermophoretic velocity.

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