Modelling Dynamics of ZnO Particles in The Spray Pyrolisis Reactor Tube

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Abstract— Development of ZnO particles research is current quite rapidly, especially in the fields of medicine and energy. ZnO Particle morphology during the process of synthesis using spray pyrolysis systems highly influential in its application the future. Our research group has developed a system of tubes spray pyrolysis reactor with the electrical heater. Physical phenomena that occur in the processing of particles, simulated in the form of a mathematical equation, useful for the experimental spray pyrolysis as there some parameters such as carrier gas flow (Q), the temperature of reactor walls (Tw), the number concentration of droplets that enter reactor (No), and the size of initial droplet diameter (dPo). The modelling parameters provide system optimization and prediction of particle morphology formed from experiments.

Keywords— Modelling, spray pyrolisis, ZnO.

INTRODUCTION

Spray method is one method synthesis of nanostructured particles is now being developed by researchers. the spray is generating small droplets derived from the liquid phase medium. The method commonly used in the synthesis of nanostructured particulate solids is spray drying and spray pyrolysis. Methods will be initiated from methyl nitrate solution or other solutions are atomised, then after passing the heating system, the solid particles will be formed according to the desired. Spray method has many advantages, including; spherical shaped particles produced, distribution of uniform diameter and can be controlled from the micrometre to sub- micrometer, better purity of the particles produced, and the continuously lasts process.

New theories about the material at the atomic scale facilitate researchers to predict the behaviour of materials at the macroscopic scale. modeling is useful for experiments in experimental spray pyrolysis because there are some parameters such as the carrier gas flow (Q), the reactor wall of Temperature (Tw), the initial concentration of the droplet solution (Co), the number concentration of droplets that enter the reactor (No.) and the size of the initial droplet diameter (dpo) that affect length of the reactor needed for the droplet becomes dry particles, final droplet size, the number of water vapor concentration in the surface of the droplet, the number water vapor concentration in the air around the droplet. the temperature on the surface of the droplet and the air temperature around the droplet, therefore, modelling varied these parameters in advance, so that later can predict the results obtained and can be used as a reference for spray pyrolysis experiments.

Specific particles required physical-chemical properties in the synthesis applications aerosols and thin films particles. To describe the process of aerosol theoretically several process variables such as precursors (base material) and the characteristics of the product should be considered. For characteristics particle that must be considered is the average size, the size of distribution, concentration, surface area, morphology, density, chemical composition, expansion of the agglomeration, optical properties, and other parameters. However those qualities are not sufficient to describe the material. Control of the aerosol processes for the production of material with the properties mentioned above also requires an understanding of the interaction between two components of aerosols: gas and particle.

EXPERIMENTAL AND MODELLING METHODE

Spray pyrolysis method is a process of forming solid particles by passing atomize / solution in the form of droplets into the heater, result of heating in reactor then solution evaporates and the solute particles will form a solid. There are four major systems in the method of spray; 1. Fluid flow system (carrier gas). This system serves as the driving droplet so can flow into the reactor, 2 Spray system. This system serves as a producer of atomization / solution in the form of droplets, 3 The heating system. The function of the heating system is to eliminate solvents (surfactant or another solvent is water) to form solid particles, 4 Particle trap system.

Our research group build spray pyrolysis reactor is made vertically, taking into account the rules and flow droplet evaporation the expected results droplet stable and doesnt turbulence. Additionally vertically installation system requires less area. The schematic of the reactor spray pyrolysis can be seen in Figure 1.

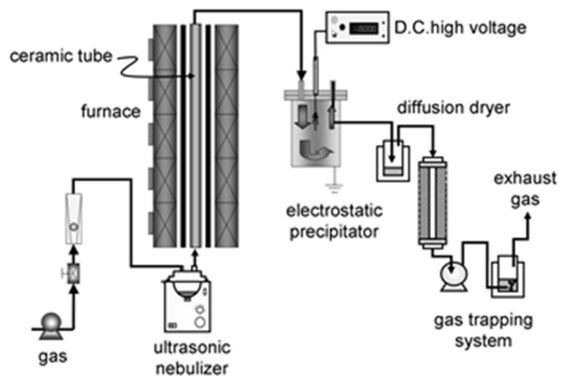

Figure 1 Schematic spray pyrolysis reactor system

Research droplet evaporation and precipitation processes of particles in the reactor illustrated in Figure 2. The model this process describe the change in diameter of the droplet and particle morphology sustained by evaporation of multiple aerosol droplets along the tubular reactor, and along with the concentration distribution of the solution in the droplet. One droplet (monodispersed droplets) having a diameter d_p, droplets concentration N_o and solution concentration C_o. These droplets are inserted into the reactor using a carrier gas stream on average Q, relative humidity RH^0 and the initial temperature T_o. Reactor with a length L and diameter 2R and has a temperature T_w. During the solvent evaporates, droplets size decreases and the concentration of the solution in increasing while moving inside the reactor. The concentration of the solution in droplets is in the critical region when the nucleation events solution, precipitation, decomposition and solid process that occurs in the particle.

Figure 2 displays schema changes in the solution concentration in droplets during evaporation of the solvent

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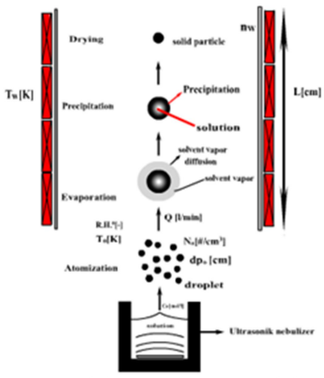

Figure 2. Overview of the simulation model

Diameter changes every time silent throughout the reactor can be stated as follows,

$$\frac{ddp}{dt} = \frac{4D_v m_l}{\rho_p dp N_A}(n - n_s) \quad (1)$$

With D_v (cm²/s) is the diffusion coefficient of vapor in the air at T, m_l (g/mol) is the molecular mass of water, n is the vapor concentration (molecules/cm^3) in the air, n_s is the vapor concentration (molecules/cm^3) on the surface T_s of the droplets and ρ_p is the density of the droplet, which is a function of particle size. T_s droplets temperature changes every time silent throughout the reactor is given by the latent heat of vaporization of water and transfer heat from the air that surrounds.

$$\frac{dTs}{dt} = \frac{1}{C_p d_p}\left[3H_L \frac{dd_p}{dt} + \frac{6h_s}{\rho_p}(T - T_s)\right] \quad (2)$$

C_p the heat capacity of droplets, H_L the latent heat of vaporisation of water and h_s the heat transfer coefficient around the droplet.

Changes in water vapour concentration against residence time is given by:

$$\frac{dn}{dt} = \left[-2\pi l_p D_V N_o (n - n_s) - \frac{2K_m(n - n_w)}{R}\right] \quad (3)$$

N_o (no/cm^3) is the number of droplet concentration, n_w is vapour concentrations in the reactor wall, and K_m is the mass transfer coefficient vapour for laminar flow, Equation (3) states that concentrations of water vapour in the air due to the evaporation of the droplet.

Temperatures on the idle time due to heat transfer from the air to the droplet and the wall of the reactor,

$$\frac{dT}{dt} = \frac{1}{FC_{pa}}\left[-\pi^2 R^2 {d_p}^2 N_o h_s (T - T_s) + 2\pi R h_w (T_w - T)\right]\left(\frac{dz}{dt}\right) \quad (4)$$

with F in Equation 4, is the average molar flow of air, C_{pa} is the heat capacity of the air is moist and h_w is the coefficient of heat transfer in the reactor wall.

By using the ideal gas law, the idle time of aerosols throughout the reactor can be stated as follows:

$$\frac{dt}{dz} = \frac{0.06\pi R^2}{Q}\left(\frac{To}{T}\right)\frac{(1 - yw)}{(1 - yw_o)} \quad (5)$$

t (s) the waiting time (s), z (cm) z are coordinates within the reactor, Q (cm^3/s) is the average air flow, T (K) is the air temperature, y_w is the mole fraction of water vapour in the air, y_{wo} is the mole fraction of water vapour in the air at z=0. The correction factor $\frac{(1-yw)}{1-yw_o}$ calculated for changes in water vapour contained in the air stream as a result of the evaporation of the droplet.

With assumes n_w=0, the mole fraction of water vapour in
the air can be declared as:

$$yw = \frac{n}{n + n_s}$$

$$yw_o = \frac{n_o}{n_o + n_s} \quad (6)$$

Equation (1) to (5) is coupled differential equations(there is linkage equation with each other equations). Authors looking for a solution to the equations simultaneously using Runge-Kutta method of order 4 with help of MATLAB program.

Runge-Kutta method of order 4 is one method for finding the solution of first order differential equations. Constants used in the model obtained from the reference and partly calculated by reference to the attachment. Term limits mass transfer and energy to the walls of the reactor is determined by the reactor system. In the case of diffusion drying, the reactor tube wrapped with "agent" Dryer so the wall behaves as perfect 'sinks' for vapour n (n_w), and the constant wall temperature. The initial condition at the reactor inlet (z = 0) is: t = 0, $d_p = d_{po}$, $n = n_o$, and $T_s = T = T_o$. The initial concentration of water vapor with relative humidity (RH^o):

$$n_o = \frac{RH^o p_s^o}{kT_o} \quad (7)$$

With p_S^o is the equilibrium vapor pressure of water at a temperature T_o and k is the Boltzmann constant. The concentration of water vapour on the surface of the droplet is given by:

$$n_s = \frac{p_s}{kT_s} \quad (8)$$

with p_s is the vapour pressure at the droplet surface temperature T_s. Presence dissolved substances in water, produce the lowest vapor pressure balance through a pure solution rather than through pure solvent $p_s^o(T_s)$:

$$p_s{}^o(T_s) = a p_s{}^o(T_s) \quad (9)$$

with a is the activity of water in the solution droplets are affected by molality solution m and osmotic coefficient of water ϕ:

$$a = \exp(-0.036 m\phi) \quad (10)$$

with ϕ is a function that alternately from which can be seen in appendix.

Assuming solution ideal mix of soluble and water droplet density is given by:

$$\rho_p = \rho_L + \left(\frac{d_{ps}}{d_p}\right)^3 (\rho_s - \rho_L) \quad (11)$$

with ρ_L is the density of pure water, ρ_s is the density of dissolved and d_{ps} is a blend of ball diameter of the drying droplet complete. Molality average droplet given:

$$m = \frac{1000\rho_s}{M_s \rho_L [(d_p/d_{ps}) - 1]} \quad (12)$$

with M_s is the molecular weight of the dissolved (ZnO).

In relation to the transport of a larger barrier to diffusion of solution in the droplet compared to solvent evaporation on the surface of the droplet, the concentration profile spreads in droplets with the highest concentration of the solution on the surface.

With assumption $d_p(dd/dt)$ is a constant, hence concentration c in the radial direction r from the center of the droplet is[1]:

$$c = c_o \exp\left[\left(\frac{K}{4D_L}\right)\left(\frac{r}{r_p}\right)^2\right], \quad (13)$$

With c_o is the concentration at the centre of the droplet, r_p=d_p/2 is the radius of the droplet, D_L is the diffusion

coefficient of solution while K is the mass balance on the surface of the droplet:

$$K = \frac{2D_v m_l (n_s - n)}{\rho_p N_A} \quad (14)$$

Because of this research reactors direction vertical upward, the authors consider the effect of gravity experienced by the droplet particlesDroplet is a particle in the form of aerosol has a mass, therefore, the effects of gravity were working on a droplet. The interaction between aerosol particles and a carrier gas can be explained by Stokes's law. Drag on particles that travel through the fluid is expressed as

$$F_D = 3\pi\mu d_p V_p \quad (15)$$

With F_D *is drag force.*

Because the particles are moving upwards, the forces acting on the particle is:

$$\sum F = 0$$
$$F_D + F_g = 0$$
$$F_D = -F_g \quad (16)$$

Then enter the definition F_D and F_g to equation 16, so that the equation 16 be:

$$3\pi\mu d_p V_p = -mg \quad (17)$$

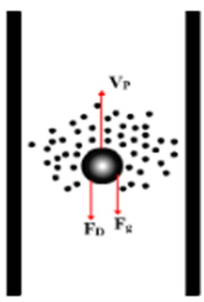

Figure 3. Scheme of the forces work on the particle

Particle velocity can be determined from the equation 17,

$$V_p = -\frac{\rho_p d_p^{\,2} g}{18\mu} \quad (18)$$

with ρ_p is the density of the droplet, is the droplet diameter, μ is the dynamic viscosity of the carrier gas, V_p is the velocity of the particle.

Particle velocity will be summed with the speed obtained from equation 4 (residence time equation), so that the particle velocity equation becomes:

$$\frac{dz}{dt} = \frac{Q}{0.06\pi R^2}\left(\frac{T}{To}\right)\frac{(1-yw_o)}{(1-yw)} - \frac{\rho_p d_p^{\,2} g}{18\mu} \quad (19)$$

Validation of modelling the data obtained by performing experiments in the manufacture of ZnO by spray pyrolysis method. Synthesis is done by using the same parameters as modelling, such as temperature reactor 800^0K, C_o initial concentration 2 mol/L, and the air flow rate Q for 10 l/min. After the ZnO particles obtained were characterized by using XRD (X-ray diffraction), to determine the structure of crystals formed After the ZnO particle characterization XRD and SEM characterization (scanning elektron microscope) to determine the size of the particles formed from the synthesis spray pyrolysis.

RESULTS AND DISCUSSION

Flow rate is an average flow of carrier gas has the unit (l/min). Flow rate was varied to three values : 1 l/min, 5 l/min, and 10 l/min. Effects of gas flow to the average droplet size evolution throughout the reactor ZnO can be seen in Figure 4.

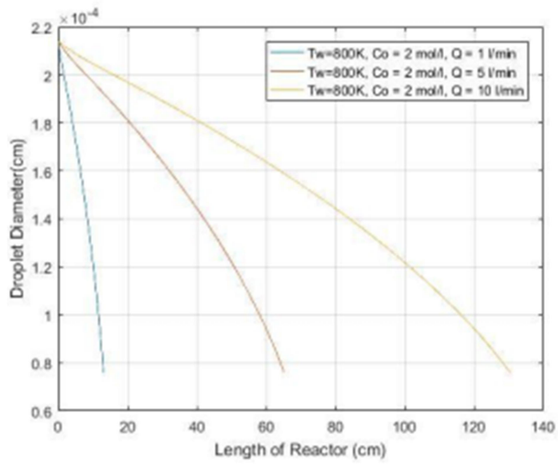

Figure 4 *The effect of flow rate on the evolution of droplet size throughout the reactor ZnO*

Based on Figure 4.1, the size of the droplet diameter evolves from 2.14×10^{-4} cm (the size of the calculation in the initial droplet nebuliser ultrasonic frequency in 1.7 MHz) until $7{,}5\times10^{-5}$ cm. The difference in length of the reactor needed to reach the final droplet size due to differences in flow rate of carrier gas that brings droplet. The greater the value of *Q*, the faster the carrier gas flow so that the evaporation same time the required length different reactors. the larger the Q value, the longer the reactor needed droplet to evaporate the solvent completely and become dry particles.

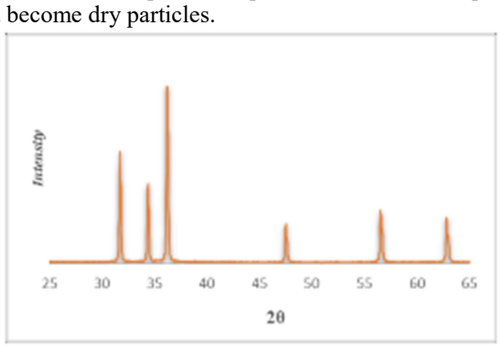

Figure 5. *The XRD pattern of ZnO at a temperature of 800^0K*

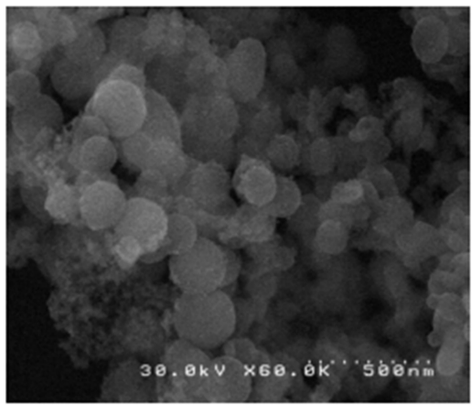

Figure 5. *SEM characterization results on ZnO particles*

CONCLUSION

Have successfully simulated the dynamics of the morphology of ZnO particles which are influenced by macro scale involved, such as the temperature of the reactor wall (T_w), the average flow rate of the carrier gas (Q), initial droplet size (d_{po}), initial concentration of ZnO solution (C_o) and the concentration of droplets into the reactor (N_o).

Diameter droplet size data validation results of the experiment and the simulation results have approximately equal size, This is because the simulation constants-constants derived from literature instead of the actual

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measurement, in addition to modelling made on the condition that modest yet the condition is real and there are still some physical phenomena other neglected in this modelling, for example, is an event agglomeration

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