Available online at www.sciencedirect.com
ScienceDirect
Computers and Chemical Engineering 31 (2007) 1088–1099
Computers & Chemical Engineering
www.elsevier.com/locate/compchemeng

A dimensionless study of the evaporation and drying stages in spray pyrolysis

N. Reuge, B. Caussat *

Laboratoire de Génie Chimique/ENSIACET/INPT, UMR CNRS 5503, 5 rue Paulin Talabot, BP1301, 31106 Toulouse Cédex 1, France

Received 17 March 2006; received in revised form 1 September 2006; accepted 25 September 2006
Available online 7 November 2006

Abstract

An original dimensionless study of the pure evaporation and precipitation stages of a spray pyrolysis process has been performed. An estimation of the evaporation time is proposed and the influence of the main processing parameters has been investigated. For operating conditions corresponding to industrial requirements, the main limiting step of the evaporation stage is thermal transfer from the column walls to the gas, not mass or thermal transfer at the droplet surface. Therefore, gas and liquid temperatures remain equal and constitutive equations can be greatly simplified. Moreover, in these conditions, neither solute concentration nor temperature gradients exist inside micronic droplets. Some data from the literature have been modelled and show the large range of validity of the equations and explanations proposed. Finally, with the assumptions made here, the dimensionless study of the precipitation stage shows that the presence of a crust can increase the drying time four-fold. However, a filled particle can still be formed.

Keywords: Spray pyrolysis; Drying; Modelling; Dimensionless study; Precipitation; Hollow particles

1. Introduction

Spray pyrolysis (SP) is an aerosol process commonly used to produce a wide variety of materials in powder form (Gurav, Kodas, Pluym, & Xiong, 1993; Pratsinis & Vemury, 1996) including metals, metal oxides, ceramics, superconductors, fullerenes and nanostructured materials. The technology has been used for many years in the materials, chemicals and food industries. It consists in five main steps: (i) generation of a spray from a liquid precursor by an appropriate droplet generator, (ii) spray transport by air flow during which solvent evaporation occurs then concomitant solute precipitation when the solubility limit is exceeded in the droplets, (iii) thermolysis of the precipitated particles at higher temperatures to form micro/nanoporous particles, (iv) intra-particle sintering to form dense particles, (v) finally, extraction of the particles from the gas flow. SP offers specific advantages over conventional material processing techniques (Gurav et al., 1993; Pratsinis & Vemury, 1996) (gas-to-particle conversion processes, liquid or solid-state processing followed by milling), such as a higher purity of the powders produced, a more uniform chemical composition, a narrower size distribution, a better regularity in shape and the synthesis of multi-component materials. Another advantage is the relative simplicity of the process, which allows easy scale-up (Joffin, 2004).

However, challenges still exist for SP, e.g. to increase production rates, to better understand the influence of the operating conditions or to control particle size, shape and internal morphology, ... Three main types of particle morphology can be obtained: (i) completely filled or "solid" nanoporous particles, (ii) microporous particles and (iii) hollow (shell-like) particles. For instance, Lyons, Ortega, Wang, and Kodas (1992) obtained hollow MgO and ZnO particles and full Al_2O_3 particles from nitrate salt precursors. No change in particle size or morphology was observed in nitrate-derived ZnO or MgO by modifying the initial air humidity or the heating rate. The addition of small amounts of seed particles with or without (i) an initially saturated drying environment and (ii) temperature gradient modifications in the flow system also had no effect. However, Lengorro, Hata, and Iskandar (2000) observed a radical change in the morphology of ZrO_2 particles with a diameter of about 3 μm, from hollow

* Corresponding author. Tel.: +33 5 34615211; fax: +33 5 34615253.
E-mail addresses: reuge@free.fr (N. Reuge), Brigitte.Caussat@ensiacet.fr (B. Caussat).

0098-1354/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compchemeng.2006.09.011

Nomenclature

a_w	water activity
Cp	specific heat (J kg^{-1} K^{-1})
c_s	solute concentration in droplet (mol m^{-3})
$c_{s,0}$	solute concentration in the initial solution (mol m^{-3})
c_s^{css}	critical super saturation concentration of the solute (mol m^{-3})
$\Delta c/c$	defined by relation (21)
D_{cr}	diffusivity of vapour through the crust (m^2 s^{-1})
D_v	binary diffusion coefficient of air/water vapour (m^2 s^{-1})
$D_{w,s}$	binary diffusion coefficient of solute/liquid water (m^2 s^{-1})
D_v^p	apparent diffusion coefficient of water vapour through the crust (m^2 s^{-1})
F	mass flow rate (kg s^{-1})
h_{vap}	vapourization enthalpy of water (J kg^{-1})
H	total distance required for the evaporation stage (m)
K	constant defined by relation (15) (m^2 s^{-1})
M	molar weight (kg mol^{-1})
P_{sat}	saturation pressure of water vapour in air (Pa)
P_1, P_2	dimensionless numbers defined by relations (7)
P_3	dimensionless number defined by relation (20)
P_4	dimensionless number defined by relation (26)
P_5	dimensionless number defined by relation (33)
q	heat flux density transferred from the column wall to the spray (W m^{-2})
q^*	dimensionless heat flux defined by relation (6)
r	distance along droplet/particle radius (m)
r_{int}	position of air/liquid interface along droplet/particle radius (m)
R	droplet radius (m)
R_c	column radius (m)
R_p	droplet radius at the onset of precipitation (m)
R^*	relative droplet radius (m)
R_p^{0D}	droplet radius at the onset of a volume precipitation (m)
s^*	parameter defined by relation (33)
t	time (s)
t_{evap}	total time of evaporation (s)
t_{drying}	total time of particle drying (s)
t_v	characteristic time of diffusion of water vapour in air (s)
$t_{w,s}$	characteristic time of diffusion of solute/water (s)
T	temperature (K)
T^*	relative temperature defined by relation (6)
v_z	mean gas velocity along reactor axis (m s^{-1})
w_a, w_w^{vap}	mass fractions of air/water vapour in gas
w_s^{liq}	mass fraction of solute in droplet
w_w^{liq}	mass fraction of liquid water in droplet
X, Y	relative mass fractions defined by relation (1)
Y_{int}	defined by relation (A.5)
ΔY	defined by relation (3)
z	axial coordinate (m)
z^*	relative axial distance defined by relation (6)

Greek symbols

α	thermal diffusivity (m^2 s^{-1})
β_c	parameter defined by relation (18)
ε	porosity of the crust
λ	thermal conductivity (W m^{-1} K^{-1})
ρ	density (kg m^{-3})
$\tilde{\rho}$	mean density (kg m^{-3})
τ	tortuosity of the crust
χ	parameter defined by relation (33)

Subscripts

a	air
d	droplet
gas	gas
liq	liquid
p	precipitate
s	solute
w	water
0	initial value

to completely filled spheres, by changing the process temperature.

Concerning the evaporation stage, some characteristic dimensionless numbers have already been used by Lyons et al. (1992), Xiong and Kodas (1993) and Sano and Keey (1982) to briefly introduce or interpret their modelling results. A more detailed dimensionless description has been performed by Jayanthi, Zhang, and Messing (1993), but only regarding their own processing conditions. It appears that ratios of characteristic times of water vapour diffusion in air, of solute diffusion in water or of thermal diffusion in the solution and the total evaporation time are key dimensionless parameters to understand the phenomena occurring in the gas and in the liquid phases. But most of these dimensionless investigations only consider individual droplets and not the global behaviour of a spray.

Moreover, the precipitation/evaporation stage, also called the drying stage (Messing, Zhang, & Jayanthi, 1993), has not been really seriously studied, excepted by Nesic and Vodnik (1991): from experiments and numerical investigations, they succeeded in finding a good model to describe the diffusion of evaporating water through the particle crust.

In the present work, in a first part an exhaustive dimensionless study of the evaporation stage was carried out in a general way. The aim was to determine the influence of each operating parameter on the process and the main limiting steps for a wide range of processing conditions. We first assume uniform solute concentrations inside the droplets and estimate in particular the evaporation time, the difference between water vapour partial pressures in air and at the droplet surface and the difference between gas and liquid temperatures as a function of processing conditions.