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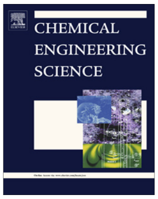

Non-isothermal population balance model of the formation and dissociation of gas hydrates

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ABSTRACT

Data reduction processes based on laboratory-scale experiments related to hydrate formation and dissociation kinetics usually employ isothermal models where the hydrate particles and continuous phase are at the same constant temperature despite the large latent heat in this phase change phenomenon. In this study, we tested this hypothesis by developing a non-isothermal model of methane hydrate formation and dissociation in a three-phase agitated vessel with a cooling jacket. The hydrate particle mass and energy comprised the distribution variables in a bivariate population balance model, which included particle nucleation, growth, breakage, and aggregation. The mass and energy balances in the gas and liquid phases completed the model. The heat transfer between the liquid phase and the coolant in the jacket was also modeled. Under the conditions analyzed, the results showed that the particle temperatures were quite close to that of the liquid phase but large changes occurred during hydrate formation or dissociation due to the slow heat transfer to the cooling fluid. Therefore, hydrate formation or dissociation occur in a environment with a changing temperature, which must be considered to obtain meaningful kinetic data.

1. Introduction

Hydrate formation and dissociation have been studied widely in the petroleum industry due to their large negative effects on flow assurance, especially during production from deep water offshore fields. Understanding these processes and their dependency on flow dynamics are a challenge for researchers when developing robust models that can simulate them in a multiphase flow (Ribeiro and Lage, 2008).

Several experimental kinetic models have been proposed for hydrate formation in well-mixed batch reactors, e.g., ZareNezhad et al. (2015) and Khosharay et al. (2015), as well as in circulating flow reactors, e.g., Odukoya and Naterer (2015) and Prah and Yun (2016). Most of these studies investigated the influence of mass transport limitation and the intrinsic kinetic rate of hydrate formation (Ou et al., 2016), where the operating pressure, temperature, stirring speed, and the geometry and dimensions of the system were the main variables considered. However, the possible heat transfer limitation on hydrate formation was usually neglected by assuming that the temperature is time and phase independent. DuQuesnay et al. (2016) studied the influence of the presence of a temperature gradient in a reactor on hydrate formation and dissociation, and showed that temperature gradients of 1.3–3.8 K were sufficient to induce a substantial variation in the hydrate's morphology and growth rate. Similar results were also obtained in other studies (Sloan and Koh, 2008) of non-mixed systems, but few studies (Bai et al., 2010; Hashemi et al., 2007; Mu et al., 2014; Odukoya and Naterer, 2015; Prah and Yun, 2016) have suggested the use of a simplified model to consider the effect of heat transfer limitation on hydrate formation.

The usual reason for neglecting the heat transfer among the phases when modeling hydrate formation in a stirred vessel is the complexity of describing polydispersed systems. Englezos et al. (1987) and Herri et al. (1999a) suggested that the dynamics of hydrate particles should be modeled based on the population balance by using the particle size only as the distribution variable. In addition, in order to consider the differences in temperature between crystals with different sizes and the liquid phase, the particle's internal energy must be considered as another distribution variable. To the best of our knowledge, this bivariate population balance model has never been applied to hydrate formation.

ZareNezhad et al. (2015) performed an experimental and theoretical study of gas hydrate formation kinetics, where they conducted experiments in a stirred jacketed reactor under isobaric and isochoric conditions. The isothermal population balance model

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Nomenclature

n^*	number of building units required to in form a hydrate core
$\mathfrak{a}$	domain-integrated aggregation frequency ($\mathrm{m}^3\ \mathrm{s}^{-1}$)
$\mathfrak{a}_{col}$	collision frequency ($\mathrm{m}^3\ \mathrm{s}^{-1}$)
A_g	aggregation source term ($\mathrm{m}^{-3}\ \mathrm{kg}^{-1}\ \mathrm{J}^{-1}\ \mathrm{s}^{-1}$)
$A_{int}^{(G-L)}$	total area of $G-L$ interface (m^2)
a_p	particle surface area (m^2)
ARE	average relative error (%)
$A_{reactor}$	reactor heat transfer area (m^2)
b	specific particle breakage rate (s^{-1})
$C_i^{(j)}$	species *i* concentration in phase *j* ($\mathrm{kg/m}^3$)
$\hat{c}_{p,i}^{(j)}$	specific heat of species *i* in phase *j* (J/kg K)
$\mathfrak{c}_q$	experimental constant ($\mathrm{m}^{-1}\ \mathrm{s}^{\mathfrak{y}-1}$)
D	impeller diameter (m)
d_{32}	Sauter diameter (μm)
$\mathfrak{D}$	methane diffusivity (m^2/s)
$d_{p,i}$	particle diameter in class *i* (m)
D_T	reactor diameter (m)
E	particle energy (J)
$\dot{E}$	rate of change of particle energy (J/s)
E_S	total energy associated with solid phase (J)
f	number density distribution function ($\mathrm{m}^{-3}\ \mathrm{kg}^{-1}\ \mathrm{J}^{-1}$)
$\mathcal{G}$	growth source term ($\mathrm{m}^{-3}\ \mathrm{kg}^{-1}\ \mathrm{J}^{-1}\ \mathrm{s}^{-1}$)
H	reactor height (m)
h	convective heat transfer coefficient ($\mathrm{W/m}^2\ \mathrm{K}$)
$H_i^{(\beta)}$	specific enthalpy of component *i* in β stream (J/kg)
$H_{i,imp}$	distance between the impeller and bottom of the reactor (m)
H_L	suspension height column (m)
$H_{s,imp}$	suspension height column above impeller (m)
$\overline{\mathcal{H}}_T$	total average source of particles ($\mathrm{m}^{-3}\ \mathrm{kg}^{-1}\ \mathrm{J}^{-1}\ \mathrm{s}^{-1}$)
J	nucleation source term ($\mathrm{m}^{-3}\ \mathrm{kg}^{-1}\ \mathrm{J}^{-1}\ \mathrm{s}^{-1}$)
J_{nuc}	nucleation rate ($\mathrm{m}^{-3}\ \mathrm{s}^{-1}$)
k	thermal conductivity (W/m K)
k_B	Boltzmann constant ($1.3806503 \times 10^{-23}$ J/K)
$k_d^{(j)}$	mass transport coefficient at interface *j* (m/s)
K^*	kinetic constant of particle growth (m/s)
L	latent heat (J/kg)
m	particle mass (kg)
$\dot{M}$	rate of change of particle mass (kg/s)
$\dot{m}_i^{(\beta)}$	mass rate of component *i* in β stream (kg/s)
$m_i^{(j)}$	mass of species *i* in phase *j* (kg)
MM	molar mass (kg/kmol)
m_S	total hydrate mass formed in the system (kg)
N	number of quadrature points
n_{CH_4}	number of molecules of host gas
$n_{\mathrm{H}_2\mathrm{O}}$	molar stoichiometric ratio
n_S	number of particles in suspension
Nu	Nusselt number (dimensionless)
P	pressure (Pa)
$\mathcal{P}$	conditional probability density function for daughter particles after breakage ($\mathrm{kg}^{-1}\ \mathrm{J}^{-1}$)
Pr	Prandtl number (dimensionless)
$\mathcal{Q}$	breakage source term ($\mathrm{m}^{-3}\ \mathrm{kg}^{-1}\ \mathrm{J}^{-1}\ \mathrm{s}^{-1}$)
$\dot{Q}^{(j)}$	heat rate across interface *j* or related to process *j* (J/s)
$\mathbf{r}$	vector of external variables
R	cylindrical reactor radial coordinate (m)
RE	relative error (%)
Re	Reynolds number (dimensionless)
s_{sur}	superficial renovation rate (s^{-1})
T	temperature (K)
T_S	average temperature of solid phase (K)
t	time (s)
U	global heat transfer coefficient ($\mathrm{W/m}^2\ \mathrm{K}$)
$\mathcal{V}_{\mathfrak{a}}$	particle volume (m^3)
$\mathcal{V}_{cell}$	cell volume (m^3)
V_H	solid phase volume (m^3)
V_L	liquid phase volume (m^3)
V_r	suspension volume (m^3)
V_{re}	reactor volume (m^3)
$\mathcal{V}_{uc}$	building unit volume (m^3)
w	impeller rotation speed (s^{-1})
$\dot{\mathbf{X}}$	vector of rate of change of the internal variables
$\mathbf{x}$	vector of internal variables
$x_i^{(j)}$	molar fraction of species *i* in phase *j*
$\mathfrak{y}$	dimensionless constant that depends on the particle size and superficial properties

Greek letters

α	collision efficiency (dimensionless)
δ_D	Dirac delta function
$\dot{\gamma}$	shear rate (s^{-1})
μ	dynamic viscosity of phase (Pa s)
μ_{kl}	*kl* moment of the particle number distribution function ($\mathrm{kg}^k\ \mathrm{J}^l$)
ν	kinematic viscosity (m^2/s)
ω	quadrature weight
ρ	density ($\mathrm{kg/m}^3$)
σ	specific surface energy ($\mathrm{J/m}^2$)
$\upsilon_{\mathrm{H}_2\mathrm{O}}$	mass stoichiometric ratio (dimensionless)
$\bar{\varepsilon}$	specific turbulent energy dissipation rate in the suspension (W/kg)
ϑ	average number of daughters particles after the breakage of a particle

Subscripts

0	reference for dimensionless variables
00	related to the zeroth-order moment in both variables
calc	calculated
CH_4	methane
e	feed
ef	effective
eq	equilibrium
er	outside reactor
ex	external
exp	experimental
f	formation
H	hydrate
re	refrigeration
$\mathrm{H}_2\mathrm{O}$	water
in	internal
ir	inside reactor
nuc	nucleation
p	particle
ref	reference state
Sus	suspension

Superscripts

$*$	dimensionless
G	gas phase
$G-L$	gas–liquid interface
GL	transfer between gas and liquid phases
L	liquid phase
c	growth
n	nucleation
S	solid phase
$S-L$	solid–liquid interface
SL	solid–liquid equilibrium
SVL	solid–vapor–liquid equilibrium
VL	vapor–liquid equilibrium