Liquid-Liquid Polymerization Front under Quasiperiodic Gravitational Modulation

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Abstract. The influence of quasi-periodic gravitational modulation of polymerization front with liquid monomer and liquid polymer is studied in this paper. The model considered includes the heat equation, the equation for the concentration and the Navier-Stokes equations under the Boussinesq approximation. The linear stability analysis of the problem is conducted and by using numerical simulation, the convective instability boundary is carried out. Results obtained show that the convective instability threshold depends on the amplitudes and on the frequencies ratio of the quasi-periodic gravitational modulation. Effect of Prandtl number is also examined.

1 Introduction

Frontal polymerization is the process of converting monomer to polymer via reaction front [1]. In this paper, we study the influence of quasi-periodic (QP) gravitational modulation on the convective instability of liquid-liquid polymerization front.

The influence of convective instability on polymerization front, in the absence of vibrations, with liquid monomer and solid polymer was studied in [2] and the case of liquid polymer was examined in [3]. Other works were dedicated to analyze the effect of a periodic gravitational modulation on the convective instability with liquid-solid polymerization front in [4] and it was found that the propagation of the reaction is affected by the parameters of vibration, while the case of liquid-liquid polymerization was studied in [5] and it was concluded that, for small vibration amplitudes, the reaction front remains stable and it loses its stability for sufficiently large amplitude of vibrations. Recent works were devoted to the influence of a QP gravitational modulation on the convective instability of reaction front. For instance, the influence of the QP gravitational modulation on reaction front was examined in the case of porous media described by the Darcy equation [6]. A work was dedicated to the case of liquid-solid polymerization front in [7] using the Navier-Stokes equations instead of the Darcy equation and it was revealed that the amplitudes and the frequencies ratio influence the stability region of the reaction. Also, it was shown that for appropriate values of vibration amplitudes and increasing values of the frequencies ratio, a stabilizing effect is reached. The effect of the wave number on the reaction front was examined showing that increasing the wave number widens the stability domain.

Recently, the case of liquid-liquid polymerization front was studied in [8]. This case is different from the previous one [7] where the equation of motion is considered only after the reaction zone since the polymer is in the solid phase.

Therefor, the equation of motion is considered before and after the reaction zone because, both the monomer and the polymer are liquids. In this latter work, the Prandtl number is taken as a constant parameter. However, many studies show a significant effect of low or high Prandtl number on convective instability (see for instance [9-11] and the references therein).

This paper is devoted to study the influence of QP gravitational modulation and Prandtl number on convective instability of liquid-liquid frontal polymerization. To this end, we consider that the acceleration b acting on the fluid is given by $g + b(t)$, where g is the gravity acceleration, $b(t) = \lambda_1 \sin(\sigma_1 t) + \lambda_2 \sin(\sigma_2 t)$ and λ_1 , λ_2 and σ_1 , σ_2 are, respectively, the amplitudes and the frequencies of the QP vibrations.

The paper is organized as follows. The next section introduces the frontal polymerization model, while the interface problem is given in Section 3. The numerical investigations are carried out in Section 4 and the last section summarizes the results.

2 Frontal polymerization model

The propagation of reaction polymerization front is modelled by the following system of equations:

$$\frac{\partial T}{\partial t} + (v \cdot \nabla)T = \kappa \Delta T + qW, \quad (2.1)$$

$$\frac{\partial \alpha}{\partial t} + (v \cdot \nabla)\alpha = W, \quad (2.2)$$

$$\begin{aligned} \frac{\partial v}{\partial t} + (v \cdot \nabla)v = -\frac{1}{\rho} \nabla p + \nu \Delta v \\ + g(1 + \lambda_1 \sin(\sigma_1 t) + \lambda_2 \sin(\sigma_2 t))\beta(T - T_0)\gamma, \end{aligned} \quad (2.3)$$

$$\text{div}(v) = 0, \quad (2.4)$$

with the following boundary conditions:

$$z \rightarrow +\infty : \quad T = T_i, \quad \alpha = 0, \quad \text{and} \quad v = 0, \quad (2.5)$$

$$z \rightarrow -\infty : \quad T = T_b, \quad \alpha = 1, \quad \text{and} \quad v = 0. \quad (2.6)$$

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and the notation:

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \quad \nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right),$$

Here (x, y, z) are the spatial coordinates, $-\infty < x, y, z < +\infty$, T is the temperature, α the concentration of the reaction product, v the mean velocity, p the pressure, κ the coefficient of thermal diffusivity, q the adiabatic temperature rise, ρ an average value of density, ν the coefficient of kinematic viscosity, γ the unit vector in the z -direction (upward), β the coefficient of thermal expansion, g the gravitational acceleration, T_0 a mean value of temperature, T_i the initial temperature and $T_b = T_i + q$ is the temperature of the burned mixture. We then suppose the chemical reaction is one-step of order zero. The reaction rate is defined as follows :

$$W = k(T)\phi(\alpha), \quad \phi(\alpha) = \begin{cases} 1 & \text{if } \alpha < 1 \\ 0 & \text{if } \alpha = 1 \end{cases}.$$

The temperature dependence of the reaction rate is shown mathematically in the Arrhenius Law $k(T) = k_0 \exp(-E/R_0 T)$ [12], where k_0 is the pre-exponential factor, E the activation energy (we will assume that the activation energy is large) and R_0 the universal gas constant. We assume that the liquids are incompressible and we neglect the term of diffusivity in the concentration equation in the way that the diffusivity coefficient is very small comparing to the thermal diffusivity coefficient.

To find the dimensionless model, we introduce the dimensionless spatial variables undermentioned :

$$\begin{aligned} x_1 &= \frac{xc_1}{\kappa}, & y_1 &= \frac{yc_1}{\kappa}, & z_1 &= \frac{zc_1}{\kappa}, & t_1 &= \frac{tc_1^2}{\kappa}, \\ p_1 &= \frac{p}{c_1^2 \rho}, & c_1 &= \frac{c}{\sqrt{2}}, & v_1 &= \frac{v}{c_1}, \\ \theta &= \frac{T - T_b}{q} \quad \text{and} \quad c^2 = \frac{2k_0 \kappa R_0 T_b^2}{qE} \exp\left(-\frac{E}{R_0 T_b}\right), \end{aligned}$$

Here c represents the stationary reaction front velocity and can be calculated asymptotically for large Zeldovich number [13]. To simplify, we keep the same notation for the other variables and pressure. We can rewrite the system (2.1)-(2.4) with the two boundary conditions (2.5)-(2.6) in the following form :

$$\frac{\partial \theta}{\partial t} + (v \cdot \nabla) \theta = \Delta \theta + Z \exp\left(\frac{\theta}{Z^{-1} + \delta \theta}\right) \phi(\alpha), \quad (2.7)$$

$$\frac{\partial \alpha}{\partial t} + (v \cdot \nabla) \alpha = Z \exp\left(\frac{\theta}{Z^{-1} + \delta \theta}\right) \phi(\alpha), \quad (2.8)$$

$$\begin{aligned} \frac{\partial v}{\partial t} + (v \cdot \nabla) v &= -\nabla p + P \Delta v + PR(1 + \lambda_1 \sin(\sigma_1 t) + \lambda_2 \sin(\sigma_2 t))(\theta + \theta_0) \gamma, \\ \operatorname{div}(v) &= 0, \end{aligned} \quad (2.9) \quad (2.10)$$

with the following conditions at infinity :

$$\begin{aligned} z \rightarrow +\infty : & \quad \theta = -1, \quad \alpha = 0, \quad \text{and} \quad v = 0, \\ z \rightarrow -\infty : & \quad \theta = 0, \quad \alpha = 1, \quad \text{and} \quad v = 0. \end{aligned}$$

Here $P = \frac{\nu}{\kappa}$ is the Prandtl number, $R = g\beta q \kappa^2 / (\nu c^3)$ is the Rayleigh number, $Z = qE/R_0 T_b^2$ is the Zeldovich number, δ and θ_0 are given, respectively, by $\delta = R_0 T_b / E$ and $\theta_0 = (T_b - T_0)/q$ and $\mu = 2\kappa \sigma / c^2$.

3 The interface problem

To study the propagation of frontal polymerization reaction with a liquid reactant and liquid product, we consider the equation of motion before and after the reaction zone. This changes the jump conditions and influences the stability conditions of the reaction process. It is worthy to notice that in the case of liquid-solid polymerization front, the equation of motion is considered after the reaction zone. The linear stability analysis leads to the following interface problem :

In the liquid monomer $z > \zeta$:

$$\frac{\partial \theta}{\partial t} + (v \cdot \nabla) \theta = \Delta \theta, \quad (3.1)$$

$$\alpha = 0, \quad (3.2)$$

$$\begin{aligned} \frac{\partial v}{\partial t} + (v \cdot \nabla) v &= -\nabla p + P \Delta v + Q(1 + \lambda_1 \sin \sigma_1 t + \lambda_2 \sin \sigma_2 t)(\theta + \theta_0) \gamma, \\ \operatorname{div}(v) &= 0. \end{aligned} \quad (3.3) \quad (3.4)$$

In the liquid polymer $z < \zeta$:

$$\frac{\partial \theta}{\partial t} + (v \cdot \nabla) \theta = \Delta \theta, \quad (3.5)$$

$$\alpha = 1, \quad (3.6)$$

$$\begin{aligned} \frac{\partial v}{\partial t} + (v \cdot \nabla) v &= -\nabla p + P \Delta v + Q(1 + \lambda_1 \sin \sigma_1 t + \lambda_2 \sin \sigma_2 t)(\theta + \theta_0) \gamma, \\ \operatorname{div}(v) &= 0. \end{aligned} \quad (3.7) \quad (3.8)$$

At the interface $z = \zeta$:

$$\theta|_{\zeta=0} = \theta|_{\zeta=+0}, \quad (3.9)$$

$$\begin{aligned} \frac{\partial \theta}{\partial z} \Big|_{\zeta=0} - \frac{\partial \theta}{\partial z} \Big|_{\zeta=+0} &= \\ \left(1 + \left(\frac{\partial \zeta}{\partial x} \right)^2 + \left(\frac{\partial \zeta}{\partial y} \right)^2 \right)^{-1} \times \left(\frac{\partial \zeta}{\partial t} + v_x \frac{\partial \zeta}{\partial x} + v_y \frac{\partial \zeta}{\partial y} - v_z \right) \Big|_{\zeta} \end{aligned} \quad (3.10)$$

$$\begin{aligned} \left(\frac{\partial \theta}{\partial z} \right)^2 \Big|_{\zeta=0} - \left(\frac{\partial \theta}{\partial z} \right)^2 \Big|_{\zeta=+0} &= \\ -2Z \left(1 + \left(\frac{\partial \zeta}{\partial x} \right)^2 + \left(\frac{\partial \zeta}{\partial y} \right)^2 \right)^{-1} \int_{-\infty}^{\theta|_{\zeta}} \exp\left(\frac{\tau}{Z^{-1} + \delta \tau}\right) d\tau, \end{aligned} \quad (3.11)$$

$$v_z|_{\zeta=0} = v_z|_{\zeta=+0}, \quad (3.12)$$

$$\frac{\partial v_z}{\partial z} \Big|_{\zeta=0} = \frac{\partial v_z}{\partial z} \Big|_{\zeta=+0}, \quad (3.13)$$

$$\frac{\partial^2 v_z}{\partial z^2} \Big|_{\zeta=0} = \frac{\partial^2 v_z}{\partial z^2} \Big|_{\zeta=+0}, \quad (3.14)$$

$$\frac{\partial^3 v_z}{\partial z^3} \Big|_{\zeta=0} - \frac{\partial^3 v_z}{\partial z^3} \Big|_{\zeta=+0} = -R \left(1 + \left(\frac{\partial \zeta}{\partial x} \right)^2 + \left(\frac{\partial \zeta}{\partial y} \right)^2 \right)^{-1} \times$$

$$\left(\left(1 + \left(\frac{\partial \zeta}{\partial x} \right)^2 + \left(\frac{\partial \zeta}{\partial y} \right)^2 \right)^{-1} - 1 \right) (1 + \lambda_1 \sin(\sigma_1 t) + \lambda_2 \sin(\sigma_2 t)) \left(\frac{\partial \theta}{\partial z} \right) \Big|_{\zeta=+0}. \quad (3.15)$$

with the conditions at infinity :

$$\begin{aligned} z = -\infty : & \quad \theta = 0, \quad v = 0, \\ z = +\infty : & \quad \theta = -1, \quad v = 0. \end{aligned} \quad (3.16)$$

Fig. 1. The critical Rayleigh number versus the amplitude λ_2 for two different values of Prandtl number.

4 Numerical results

To study the stability of reaction front, we seek the solution of the problem as follows :

$$\theta = \theta_s + \tilde{\theta}, \quad p = p_s + \tilde{p}, \quad v = v_s + \tilde{v},$$

where $\tilde{\theta}$, $\tilde{p}$ and $\tilde{v}$ are respectively small perturbation of temperature, pressure and velocity.

We consider the perturbation as follows :

$$\hat{\theta}_i = \theta_i(z_2, t) \exp j(k_1 x + k_2 y),$$

$$\hat{v}_{zi} = v_{zi}(z_2, t) \exp j(k_1 x + k_2 y),$$

$$\xi = \varepsilon_1(t) \exp j(k_1 x + k_2 y),$$

where k_i , $i = 1, 2$ and ε_1 denote, respectively, the wave numbers (in x and y directions) and the amplitude of the perturbation and $j^2 = -1$.

The propagating reaction front problem can be reduced to the following system:

$$z_2 < \xi :$$

$$\begin{cases} \frac{\partial w}{\partial t} - uw' - P(w'' - k^2 w) = -Qk^2(1 + \lambda_1 \sin(\sigma_1 t) + \lambda_2 \sin(\sigma_2 t))\theta, \\ w = v'' - k^2 v, \\ \frac{\partial \theta}{\partial t} - \theta'' - u\theta' + k^2 \theta = 0. \end{cases}$$

$$z_2 > \xi :$$

$$\begin{cases} \frac{\partial w}{\partial t} - uw' - P(w'' - k^2 w) = -Qk^2(1 + \lambda_1 \sin(\sigma_1 t) + \lambda_2 \sin(\sigma_2 t))\theta, \\ w = v'' - k^2 v, \\ \frac{\partial \theta}{\partial t} - \theta'' - u\theta' + k^2 \theta = u \exp(-uz_2)v. \end{cases}$$

With the following boundary conditions :

$$\theta_2(0, t) - \theta_1(0, t) = u\varepsilon_1(t),$$

$$\theta'_2(0, t) - \theta'_1(0, t) = -u^2\varepsilon_1(t) - \varepsilon'_1(t) + v_1(0, t),$$

$$\theta'_2(0, t) + \frac{Z}{u}\theta'_1(0, t) = -u^2\varepsilon_1(t),$$

$$v_1^{(i)}(0, t) = v_2^{(i)}(0, t), \quad i = 0, 1, 2, 3.$$

By combining the boundary conditions, we get :

$$\theta'_1(0, t) + \frac{Z}{u}\theta_1(0, t) = \frac{1}{u}(\theta_2(0, t) - \theta_1(0, t))' - v_0.$$

Fig. 1 shows the critical Rayleigh number as a function of the amplitude λ_2 of QP vibrations for $k = 0.7$, $\lambda_1 = 5$, $\mu_1 = 5$, $\frac{\sigma_2}{\sigma_1} = \sqrt{2}$, $Z = 8$ and for two different values of Prandtl number. It can be observed that for increased value of Prandtl number, the reaction front loses its stability.

Fig. 2. The critical Rayleigh number versus the amplitude λ_2 for $P = 10$ and different frequencies ratio.

Fig. 3. The critical Rayleigh number versus the Prandtl number P for $\sigma_2 = \sqrt{2}\sigma_1$ and $\sigma_1 = 5$.

Fig. 2 illustrates the critical Rayleigh number versus the amplitude λ_2 for different frequencies ratio, $P = 10$, $Z = 8$, $k = 0.7$, $\lambda_1 = 5$ and $\mu_1 = 5$. From this figure we can conclude that by increasing the frequency ratio, the stability domain becomes large in certain interval of λ_2 . By comparing this figure with the results found in [8] where the Prandtl number, we can observe that by increasing the Prandtl number ($P = 10$), the frequency ratio has a destabilizing effect for small values of the amplitude λ_2 ($0 \leq \lambda_2 \leq 10$).

The critical Rayleigh number as a function of the Prandtl number P is given in Fig. 3 for $\sigma_2 = \sqrt{2}\sigma_1$, $\sigma_1 = 5$, $\lambda_1 = \lambda_2 = 5$, $Z = 8$ and $k = 0.7$. It can be concluded that, for a fixed frequency ratio, small values of the Prandtl number has a stabilizing influence on the reaction front and by increasing P , we can observe that the stability region is decreased. When the Prandtl number exceeds certain value ($P \geq 7$), the effect of this parameter on the stability of the polymerization front is negligible.

5 Conclusion

In this paper, we have studied the influence of the QP gravitational modulation on the convective instability of frontal polymerization with liquid monomer and liquid polymer. To achieve this, we have considered the model which includes the heat equation, the concentration equation and the Navier-Stokes ones under boussinesq approximation.

Assuming the polymerization reaction occurs in a small zone when the activation energy is high, we have used the Zeldovich Frank-Kamenetskii method, called also narrow zone approximation. We have performed an asymptotic analysis to establish the interface problem and the solution has been chosen as a perturbed stationary solution. The numerical results show that the convective instability strongly depends on the parameters of the QP vibrations (frequencies ratio and amplitudes) and the Prandtl number.

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