NEW APPROCHES TO MODELLING OF RAPID EXPANTION OF SUPERCRITICAL FLUIDS LEADING TO FORMATION OF NANOPARTICLES

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INTRODUCTION

The rapid expansion of a supercritical fluid containing dissolved substances is widely used for producing nano- and microparticles of solid materials [1,2]. The main RESS advantages were demonstrated in numerous experiments focused on the synthesis and production of a wide range of nanoparticles of organic and inorganic compounds [3,4].

The present work is the continuation of the earlier started works [5] aimed at detailed hydrodynamic modeling of a flow of supercritical solution – a fluid containing a solvent, dissolved substance (phenanthrene, naphthalene, etc.) and co-solvent (methanol, isopropanol, ethanol). The main task of the modeling and calculations is to determine the regularities and conditions that provide size-specific production of solid particles in expanding flow.

METHODS

Principal scheme of the rapid expansion of supercritical fluid through a capillary is presented in Fig. 1.

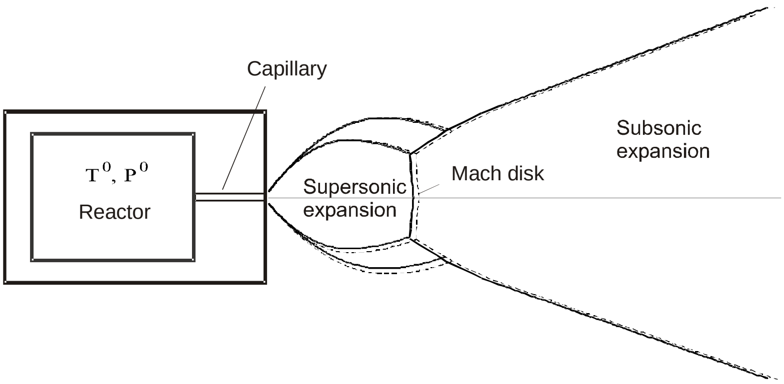

Fig. 1 Diagram of a reactor and outflow jet: I – capillary, II – supersonic flow region. III – Mach disk, IV – subsonic flow region. P_0, T_0 – pressure and temperature in the reactor; P^{∞} - external pressure; Da – capillary diameter, Dm – Mach disk diameter.

The supercritical state of the solution in the reactor is reached at temperature T^0 and pressure P^0 exceeding critical parameters of the reaction mixture. The supercritical solution is throttled through a capillary into a vessel with external pressure P^{∞} and temperature T^{∞}. Thermodynamic and hydrodynamic parameters of the outflow jet vary along the whole length of its expansion. The flow in the capillary gets faster owing to the action of friction force and reaches sonic speed at the outlet section, i.e. the Mach number goes to 1. At capillary cut, the subsonic flow turns to supersonic flow. At some distance, the supersonic flow transforms into subsonic one again. The flow transformation from supersonic to subsonic regime occurs on the Mach disk. As the subsonic flow expands, its speed decreases to zero. With decreasing pressure and temperature, the dissolved solid substance precipitates from the solution in a form of particles.

Hydrodynamic modeling of two-dimensional multi-component fluid flow with the phase separation and particle formation in nonideal-gas approximation was conducted.

Generally, mathematical model of each flow region is represented by mass, momentum and energy conservation equations set. It includes also the state equation and enthalpy equation. In general case, the two-dimensional equations set is presented as follows:

$$\frac{\partial \rho u y}{\partial x} + \frac{\partial \rho v y}{\partial y} = 0$$

$$\frac{\partial}{\partial x}\left[y\left(\rho u^2 + \frac{\gamma - 1}{2\gamma} p \right)\right] + \frac{\partial (yuv\rho)}{\partial y} = 0$$

$$W^2 + \frac{p}{\rho} = 1$$

$$\frac{dp}{dx} = -2\frac{dy_1}{dx}\left[y_1\left(\frac{1}{\gamma p} - \frac{\gamma - 1}{2\gamma}\frac{1}{\rho W^2} \right)\right]^{-1}$$

where x - coordinate; u, v – the projections of the speed vector in the cylindrical coordinate system related to the maximum speed; W – speed modulus; p, ρ - pressure and density, related to the pressure and density before shock compression; $y_1 = y_1(x)$ – equation for the tangential discontinuity line separating the flows behind the reflected and central shockwaves.

The Redlich-Kwong-Soave equation of state was used as the thermodynamic model. Mathematical models for capillary fluid flow, and the particle nucleation and growth are presented in detail in [5].

To solve the model equations, non-isobaric jet calculation method was applied, which is based on use of second-order accurate explicit difference scheme and smoothing procedure.

RESULTS

The expansion hydrodynamics of the chosen mixtures are calculated for a given capillary geometry; T^0 P^0 – temperature and pressure in the reactor, P_{inf} – external pressure. Calculation was made for the composition: propane solvent 90 mol %, methanol co-solvent 7.5 mol %, phenanthrene as dissolved substance 2.5 mol %. (mixture No. 1).

Consider the effect of the selected parameters on thermodynamic and gas-dynamic variables, and on the process of nanoparticle nucleation and growth. According to adopted calculation pattern, the effect of each parameter will be studied individually in three separate zones of fluid flow: capillary, super- and subsonic regions, and on Mach disk.

Results of complete calculation of the flow motion and stream expansion are presented in Figs. 2-4.

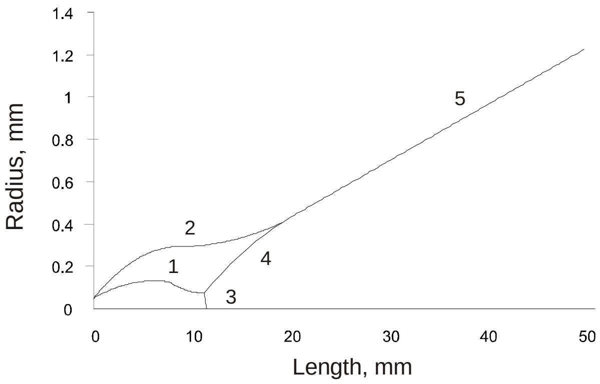

Fig. 2. Jet boundaries of mixture No. 1. 2, 5 – external boundaries; 1 – barrel shock; 3 – Mach disc; 4 – transition segment

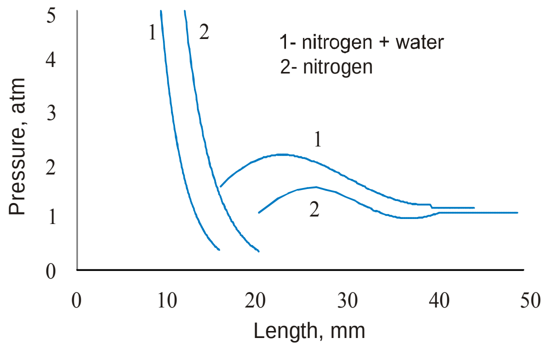

Fig. 3 Temperature profiles of the flow along the length close Mach disk

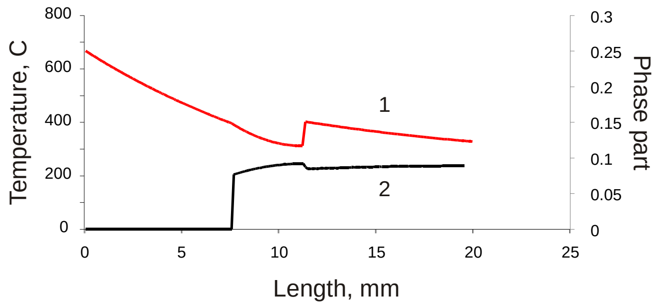

Fig. 4. Temperature -1 and the part of liquid phase -2 along the length of each region of the flow motion

By analogy with temperature profiles, Fig. 4 shows the flow rate profiles along the length of all isolated regions of the flow motion and expansion.

Temperature and composition of the mixture in the reactor entry, external pressure, as some other process parameters affect the size and distribution of the phenanthrene generated particles, see Figs. 5-7. You can see also that the radius of the expanding jet at the same distance from the capillary edge equal to 35 mm increases slightly with the temperature of the fluid in the reactor, Fig. 5, while the maximum particle size decreases by almost half.

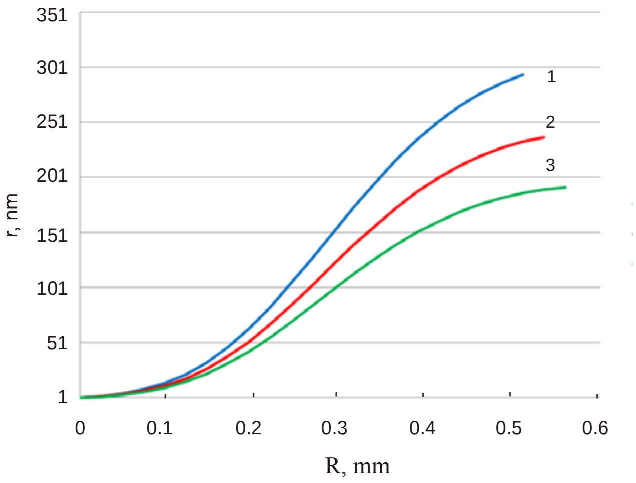

Figure 5. Effect of the temperature in the reactor at the particles size distribution in a flow on the distance from the capillary edge is 35 mm. Mixture composition in %: propane/methanol/ phenanthrene is 90/7/3, external pressure 5 atm. 1 - 500; 2 - 550; 3 - 600K. r is the radius of the particles; R is the radius of the jet.

External pressure effects even stronger on the size of the particles and their distribution, see Fig. 6. So, the increase of external pressure from 2 to 10 atm leads to the increase of the maximum particle size more than six times. This means that changing external pressure, you can easily control the size of the resulting particles. The decrease in the part of phenanthrene in the original mix by approximately 4%, Fig.7, at the corresponding increase in the share of alcohol, may reduce the maximum particle size of more than 1.5 times at almost constant size jet.

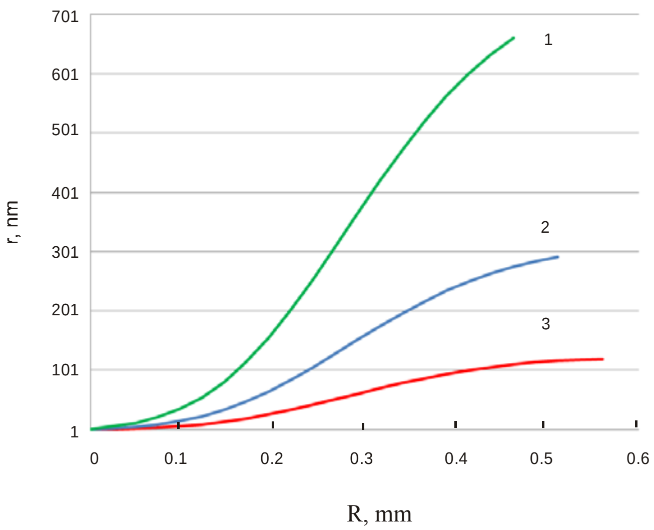

Figure 6. Effect of external pressure on the particles size distribution in a flow on the distance from the capillary edge is 35 mm. Mixture composition: propane/ methanol/ phenanthrene is 90/7/3 %, the temperature in the reactor is 500K. 1- 10 ; 2 - 5; 3 - 2 atm. r is the radius of the particles; R is the radius of the jet.

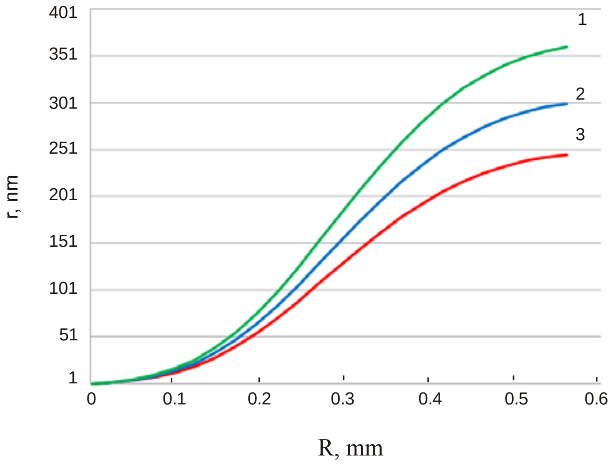

Figure 7. Effect of the mixture composition at the reactor entry on the particles size distribution in a jet flow on the distance from the edge of the capillary 35 mm. Mixture composition : propane/ methanol/ phenanthrene: 1 – 88/9/3, 2 – 90/7/3; 3 – 92/5/3; the temperature in the reactor is 500K. r is the radius of the particles; R is the radius of the jet.

CONCLUSION

Mathematic modeling of the rapid expansion of supercritical fluid containing dissolved solid component and analysis of the parametric sensitivity of the model allowed to find the most significant parameters for controlling the size and properties of the produced particles. The calculations showed that all the studied parameters of RESS process affect in one way or another the size of the formed particles that seriously complicates process optimization, on the one hand, and worsens the efficiency of comparative analysis of calculated and experimental data.

Finally, let us outline below the effect of the studied parameters on the critical nucleus radius and size of the formed particles.

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