Mathematical modeling of the rapid expansion of supercritical fluid

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Mathematical modeling of the rapid expansion of supercritical fluid leading to the formation and growth of nanoparticles of a solid substance predissolved in the fluid was performed. According to the scheme of fluid motion, the mathematical model describes three characteristic segments of the flow motion and a shock wave at the Mach disk: (1) flow in a capillary; (2) supersonic expansion of a stream; (3) flow motion in subsonic expansion region. To simulate normal shock wave, the equations of conservation of mass, momentum and enthalpy were derived. Thermophysical and thermodynamic parameters and phase state of the mixture were calculated for each isolated segment of the flow motion using the Redlich–Kwong–Soave equation of real gas state.

Algorithms and a program were developed for solving the model equations. Choice of the solving methods was determined by specificity of the flow motion and expansion in each of isolated regions. Thus, as the condition of critical outflow at the capillary outlet should be satisfied, hydrodynamics of the flow motion in a capillary was calculated by an iterative method.

Supersonic region of stream expansion is limited by the Mach disk, where all parameters of the flow undergo an abrupt change, and transition from supersonic expansion region to subsonic one occurs. In subsonic region of stream expansion the motion is isobaric, thus the geometry of supersonic region forms so that at the normal shock wave the post-shock pressure is equal to ambient pressure.

In subsonic isobaric segment of stream expansion the flow rate virtually vanishes; temperature of the flow tends to ambient temperature. A model of this segment is supplemented with the equations of nucleus formation and growth of the solid phase particles along the expansion axis.

A parametric analysis of the mathematical model showed that critical radius and size of the particles that form during rapid expansion of supercritical fluid depend both on the parameters of reactor mixture and on the capillary geometry. Size of the nascent particles can be varied in a wide range by changing the temperature and pressure of reactor and/or environment at a fixed capillary geometry. Calculation was made for the composition: CO_2 solvent 90 mol %, ethanol co-solvent 7.5 mol %, phenanthrene as dissolved substance 2.5 mol %. Effect of the mixture composition on the outflow hydrodynamics and particles growth was studied. Components of the mixture and their percentage were varied. It is worthy of note that for some compositions solution of the system does not exist. For instance, in some cases, a solid substance dissolved in supercritical CO_2 becomes

completely soluble in co-solvent under precritical conditions. We tested several co-solvents: methanol, ethanol and isopropyl alcohol, in combination with dissolved solid substances: naphthalene, biphenyl, phenanthrene and anthracene.