Summary of doctoral thesis

# Preparation, properties and applications of nanofluids with multi-walled carbon nanotubes and biopolyols

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The development of electronics, the miniaturization of devices, rapid changes in the transportation sector or the shift away from fossil fuels are prompting the search for new solutions related to optimal heat management. Nanofluids are meeting the high demands placed on heat transfer fluids. Nanofluids make it possible to increase the efficiency of electronic devices, extend the operating time of cells in electric cars, efficiently receive heat in industrial, solar or geothermal heat pumps. A characteristic feature of nanofluids is their high thermal conductivity, compared to conventional heat transfer fluids, for which nanoparticles dispersed in the base fluid are responsible. Despite their better thermal properties, nanofluids still have not found a viable application in industry. One of the main reasons for this is the lack of sedimentation stability and changes in the values of physicochemical parameters over time. Moreover, the large-scale production process design and the safety of their use are also challenges.

The subject of this doctoral dissertation is the 56 nanofluids, composed of 7 base liquids (1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2,3-propanotriol and equimolar mixtures of 1,2-ethanediol with 1,2,3-propanotriol, 1,2-propanediol with 1,2,3-propanotriol and 1,3-propanediol with 1,2,3-propanotriol), 2 types of multiwalled carbon nanotubes (MWCNTs) k-MWCNTs (outer diameter 50-80 nm, length 0.5-2.0 µm) and d-MWCNTs (diameter 60-80 nm, nominal length 770 µm), and a poly(*N*-vinylpyrrolidone) stabilizer with an average molecular weight of 40 kDa (PVP40). All of the developed nanofluids are characterized by long-term sedimentation stability, which is up to 4 years for selected samples, and higher thermal conductivity compared to the base fluids. The highest increases in thermal conductivity of 38% and 37% at 298.15 K were obtained for nanofluids containing 1.00 wt.% d-MWCNTs, in which the base liquid was 1,2-propanediol and an equimolar mixture of 1,3-propanediol with 1,2,3-propanotriol, respectively. The obtained enhancement in thermal conductivity is significantly higher than those reported in the literature for the same temperature, base liquid and the same or similar MWCNTs content.

The stability examination included the visual observation, centrifugation tests, as well as measurements of density and thermal conductivity at time intervals. The density and thermal conductivity of the nanofluids were measured after time intervals ranging from 7 to 37 months, and it was shown that the changes in values were no more than 0.06% and 3.0%, respectively.

Within the framework of the present work, compositions and a method for obtaining long-term stable nanofluids were developed, and physicochemical properties of the obtained nanofluids such as density, thermal conductivity, dynamic viscosity, and isobaric heat capacity were studied. Using the measured quantities for nanofluids characterized by the greatest increase in thermal conductivity, Prandtl number, thermal diffusivity and volumetric isobaric heat capacity were calculated and compared with the properties of commercially available heat transfer fluids DOWCAL™100, based on 1,2-ethanediol, and DOWCAL™200 and DOWCAL™N, based on 1,2-propanediol. It was concluded, based on a comparative analysis, that the studied nanofluids have a higher thermal energy storage capacity than commercially available working fluids, allow for more efficient heat transport, and enable a reduction in the volume of heat transfer fluid in the system without reducing the efficiency of the heating or cooling process. The above features represent a significant advantage of nanofluids over conventional heat transfer fluids.

Using microimaging techniques using transmission electron microscopy (TEM) and its cryogenic version (cryo-TEM) and optical microscopy, a detailed analysis of the structure of the studied nanofluids was carried out. Based on microscopic techniques, the mechanism of steric stabilization of MWCNTs by PVP40 was elucidated. It was shown that PVP40 wraps around MWCNTs preventing them from approaching each other and aggregating. By comparative analysis, with micrographs of ionic liquid-based systems containing d-MWCNTs available in the literature, the mechanism of heat transfer through thermal bridges formed by d-MWCNTs was elucidated. In conjunction with Raman spectroscopy, the interactions occurring in the nanofluids were analyzed, including those between the base liquid, PVP40 and MWCNTs, and the base system and PVP40.

Cytotoxicity studies were performed for selected nanofluids, proving that dispersion of k-MWCNTs in 1,2-propanediol with PVP40 or in 1,3-propanediol with PVP40 reduced the toxicity of k-MWCNTs to normal human skin fibroblasts. This represents an important result in terms of the safety of large-scale use of nanofluids.

In the last step, the scale of preparation of nanofluids was transferred to a fractional-technical scale with the possibility of scaling up to the production scale, and it was shown that the changes in density, dynamic viscosity and thermal conductivity compared to nanofluids obtained at the laboratory scale are within the measurement uncertainty for these quantities. The developed and verified method of preparation represents an important step in the applicability of nanofluids and enables their use as heat transfer fluids in industry.

At each stage of the research, the results obtained were evaluated and compared with the available scientific literature on nanofluids with MWCNTs and biopolyols.

The explanation of the mechanism of heat transfer and stability of nanofluids, based on a comprehensive study of their structure, stability and physicochemical properties, are important contributions to the discipline of chemical sciences.