148l Thermodynamic Characterization of Milspec Hydrazine

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MILSPEC hydrazine is a commonly used aerospace propellant. This grade of hydrazine has a minimum of 98.5 percent (by weight) hydrazine, the remainder impurities are mostly water. It is difficult to perform laboratory experiments with this propellant because of its toxic characteristics; therefore, it is in the interest of safety to develop chemical engineering methods to characterize this fuel. Previous work has developed methods for modeling this fuel, but is limited because the contribution of water has not been considered. Thermodynamic characterization of hydrazine is needed for use with design calculations for aerospace applications.

Development of a satisfactory equation of state to describe the phase transition between the liquid and vapor phases was investigated. A vapor pressure correlation was needed for the evaluation of an equation of state for hydrazine. Published correlations from Barragan[1] and a Giordano[2] were compared by testing each for thermodynamic consistency. The Barragan correlation was better able to predict the boiling point of hydrazine and its critical temperature and pressure. The Barragan correlation was used with published Peng-Robinson[3], Giordano[2] and Martin[4] equations of state. The equations of state were tested for thermodynamic consistency through comparison of liquid and vapor fugacity coefficients as well as mechanical stability. The Peng-Robinson equation of state predicted the most thermodynamically consistent results.

In order to investigate the vapor-liquid equilibrium of MILSPEC hydrazine the equation of state was used to perform flash calculations of a mixture of hydrazine and water. Different forms of the Peng-Robinson equations of state were evaluated using different activity coefficient models and mixing rules. Van Laar and UNIFAC activity coefficients were used along with the Wong-Sandler mixing rules.[5] Flash calculation results were compared with experimental data to determine the predictive ability of each model. The most accurate model was the PRSV-WS-UNIFAC model.[6] It performed well over the full temperature range where a phase diagram was available from the literature.[4]

The Gordon-McBride Chemical Equilibrium and Applications (GM-CEA) was used to evaluate the chemical equilibrium compositions of pure and MILSPEC combinations of hydrazine. Results from the GM-CEA program showed that the small water impurity present in MILSPEC hydrazine did not affect the equilibrium compositions of hydrazine products.

1. Barragan, M.; Woods, S.; Wilson, D. B., An Equation of State for Hydrazine and Monomethylhydrazine, Its Validation and Use for Calculation of Thermodynamic Properties. In 1998 JANNAF Propellant Development & Characterization Subcommittee (PDCS) and Safety & Environment Protection Subcommittee (S&EPS) Joint Meeting, NASA Johnson Space Center, Houston, Texas, 1998.

2. Giordano, D., Survey of the Thermodynamic Properties of Hydrazine. Journal of Chemical Engineering Data 2001, 46, (3), 486-505.

3. Sandler, S. I., Chemical and Engineering Thermodynamics. Third ed.; John Wiley and Sons, Inc.: New York, 1999; p 772.

4. Schmidt, E. W., Hydrazine and Its Derivatives: Preparation, Properties, Applications. Second Edition ed.; John Wiley and Sons, Inc.: 2001; Vol. 1 and 2, p 2121.

5. Orbey, H.; Sandler, S. I., Modeling Vapor-Liquid Equilibria: Cubic Equations of State and Their Mixing Rules. Cambridge University Press: Cambridge, 1998.

6. Mitchell, M.; Rakoff, R.; Jobe, T.; Wilson, D. B.; Saulsberry, R. In A Thermodynamic Description for MILSPEC Hydrazine, 3rd International Workshop on Hydrazine, Sardinia, Italy, 2004.