Thermal Decomposition: A Prelude to Thermophysical Property Measurements

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In recent years, the need for thermophysical property data for specific complex fluids at high temperatures and pressures has become more pressing. For example, our laboratory has been involved with rocket propellants, aviation fuels, and organic working fluids, all of which are exposed to high temperatures and pressures. Because of this, thermophysical property information has been needed at those high temperatures and pressures. There is some degree of risk in blindly filling a costly, one-of-a kind property measurement apparatus with, say, jet fuel, and operating the instrument in a region where thermal decomposition is a possibility. We have therefore developed an approach for chemical reaction screening for such fluids. Based on an ampoule reactor, the apparatus allows a fluid to be exposed to the potentially hostile conditions (of temperature and pressure) for a predetermined duration. After exposure, the sample is harvested from the ampoule and analyzed by any suitable technique. Usually a decomposition suite of products can be identified. The increase in concentration of the decomposition suite as a function of time can provide global thermal decomposition kinetics. A qualitative analysis of the decomposition suite can provide insight into the reaction mechanism. Although this approach is not a rigorous study of the complex kinetics, with all of the intermediate species and steps, it provides essential information used to guide other aspects of the measurement program. In this talk, the basic apparatus and theory will be described and case studies that include Rocket Propellant 1, JP-10, and organic Rankine cycle working fluids will be discussed.