ADVANCED REACTIVE SYSTEM SCREENING TOOL (ARSST)

James P. Burelbach
Fauske & Associates, Inc.
16W070 West 83rd St., Burr Ridge, IL, 60521, USA
Burelbach@Fauske.com

ABSTRACT

The new Advanced Reactive System Screening Tool (ARSST) is an easy-to-use and cost-effective calorimeter that can quickly and safely identify potential chemical hazards in the process industry. ARSST data yield critical experimental knowledge of the rates of temperature and pressure rise during a runaway reaction, thereby providing reliable energy and gas release rates which can be applied directly to full scale process conditions.

INTRODUCTION

Safe process design requires knowledge of chemical reaction rates, character, and energy release. The Design Institute for Emergency Relief Systems (DIERS) program *(1)*, under the auspices of the AIChE, provided the chemical process industry with tools necessary to gather such data *(2)*. A primary purpose of the effort was evaluation of emergency relief vent requirements, including energy and gas release rates for systems under upset conditions, and the effects of two-phase flow on the emergency discharge process. The Reactive System Screening Tool (RSST) later provided an easy, inexpensive approach to the DIERS procedure *(3, 4)*. The RSST has become a standard industry tool for characterizing chemical systems and acquiring relief-system design data. The RSST, along with equally easy-to-use vent sizing formulae accounting for two-phase flow *(5)* are considered well suited to the task of selecting the overall worst case scenario. This paper addresses the latest advances in RSST technology, as embodied in the recently released ARSST calorimeter *(6)*.

The ARSST retains all the capabilities of the acclaimed RSST. New Windows software features a broad range of scan rates (0-30°C/min), a heat-wait-search (HWS) mode of operation providing onset detection sensitivity as low as 0.1°C/min, and isothermal operation at elevated temperature. Endothermic behavior (phase change) is readily accommodated, and an optional *Flow Regime Detector* allows the ARSST operator to distinguish between “foamy” and “non-foamy” runaway reactions.

ARSST DESCRIPTION

The basic components of the ARSST (Figure 1) include the 10-ml open spherical glass test cell, heater, insulation, thermocouple(s), pressure transducer, and a 350-cc stainless steel containment vessel that serves as both a pressure simulator and safety vessel. A small magnetic stir bar is typically placed in the test cell and driven by an external magnetic stirrer. The external bottom heater is belted directly to the test cell. The apparatus has a low effective heat capacity relative to that of the sample, which may be expressed as a capacity ratio, or phi-factor, of about 1.04 (i.e., quite adiabatic). This key feature allows the measured data to be directly applied to process scale.

Sample temperature is measured using a type K thermocouple (stainless steel or Hastelloy sheathed, or glass encapsulated), and a 500-psig pressure transducer is standard. The containment vessel is hydrostatically tested to 3000 psig, and it has a Hastelloy rupture disk rated at about 900 psig. Containment gas temperature is readily measured during a test by using an optional second thermocouple. The containment vessel and magnetic stirrer are normally located in a chemical hood, with connections to a regulated inert gas supply and vent. The control box contains the temperature and pressure amplifiers and the heater power supply. A single heater circuit powers the 24 Ω bottom heater and delivers up to 17 W. An external fill tube can be used to add reagents to the open test cell either before or during a test, and an injection piston can be used to add reagents against elevated backpressure.

FLOW REGIME DETECTION

An exciting development, which is offered as a complement to the ARSST, is the *Flow Regime Detector*. This patented device (Figure 2) allows the ARSST operator to distinguish between "foamy" and "non-foamy" runaway reactions. It comprises a small immersion heater and an attached thermocouple that is positioned in the upper free board space of the test cell. (For Flow Regime tests the ARSST test cell is only about 1/2 full.) An auxiliary control box contains a dedicated power supply for the sensor. The detector temperature is displayed on the ARSST screen and also logged to the output data file. Prior to externally heating the chemical sample itself, power is supplied to the internal heating coil to establish an elevated sensor temperature which is well above the anticipated boiling (tempering) temperature of the sample. The detector operates on the simple principle that if the flow regime following the onset of boiling is foamy, then the detector will be wetted and rapidly cooled. If the flow regime is non-foamy, then the detector thermocouple (TC2) will continue to measure a temperature well in excess of the sample temperature (TC1). Relief systems for non-foamy systems may be more realistically designed by treating the two-phase discharge flow as churn-turbulent rather than homogeneous.

NEW SOFTWARE FEATURES

The ARSST is computer controlled using all-new operating software on a 32-bit Windows platform. The computer records time, temperature(s), pressure, and heater power during a test. Live temperature, pressure, and power histories are simultaneously displayed on the graphical interface. Convenient data reduction and plotting software quickly generate plots of temperature or pressure vs. time, temperature vs. pressure, temperature rate or pressure rate vs. inverse temperature, and heater power vs. time. All plots can be saved electronically for easy insertion into Word documents.

The new software automatically calibrates the heater/sample system for both constant ramp and adiabatic modes of operation. This provides for excellent accuracy in maintaining a specified temperature (heat up) ramp and close approximation to adiabatic conditions. Experiments can be run in the conventional way, with an imposed temperature ramp up to (and during) a runaway reaction, or in a two-stage process where each experiment consists of separate "Calibration" and "Acquisition" stages. During calibration the heater operates under PID control, but during acquisition the heater is controlled by the calibration polynomials. The test operator may (a) perform calibration on the reactive sample during a test (prior to the onset of an exotherm), (b) utilize a "saved" calibration from a previous test, (c) perform and save a "blank" calibration on a non-reactive sample (say, a solvent), or (d) input a user specified calibration (three constants required). "Standard" calibrations for selected nominal temperature ramp rates are included with the ARSST software.

Various types of experiments are possible with the ARSST. Conventional thermal scan experiments are easily run using a single ramp calibration that is either developed in-situ or saved from a previous test. Fire exposure simulations may be carried out at rates up to 30°C/min. Heat-wait-search experiments may be performed using an operator-specified series of alternating temperature ramps and plateaus; if self-heating is detected then the heater subsequently operates in adiabatic mode. The onset temperature can be detected at rates as low as 0.1°C/min, and the heat of reaction can be estimated from the adiabatic temperature rise. Exotherm detection can also be accomplished in DSC mode by performing a constant ramp rate thermal scan under PID control and comparing the power history to that for a similar non-reactive sample. This technique can be used to estimate the onset temperature at which the required power input begins dropping off. Aging experiments can be conducted by using PID control to maintain an elevated temperature for a specified period of time; subsequently a HWS or dynamic test can be run.

SAMPLE RESULTS

Several benchmark systems have been examined using the ARSST. Figure 3 shows ARSST results for 25% DTBP in toluene under 360-psig backpressure. The ARSST-HWS test was performed in heat-wait-search mode with 5°C steps. The reaction was detected at 120°C at a rate of about 0.1°C/min, and was subsequently followed in adiabatic mode. The ARSST-scan test was performed using a simple thermal scan. An initial ramp at 2°C/min was followed by heater calibration at 0.5°C/min from 60 to 100°C. Subsequently the heater was polynomial-controlled (driven) at 0.5°C/min. Also shown in Figure 3 are closed-system adiabatic data that were obtained with the VSP2 (Vent Sizing Package 2). Variations in measured peak temperatures/self-heat rates are due to toluene vapor stripping during the gas-generating peroxide decomposition. Arrhenius parameters (E_A = 38.0 kcal/mol and $\log_{10}A$ = 16.1 s^{-1}) were computed from the ARSST thermal scan data and are in good agreement with published values *(7, 8)*.

Figure 4 shows self-heat rate results for methanolysis of acetic anhydride, and again compares ARSST and closed cell VSP2 data. The ARSST test used a saved ramp polynomial that had been previously developed by heating pentadecane at 0.1°C/min. Figure 4 also illustrates excellent agreement in first-order rate constant between these two tests.

A recent DIERS round robin exercise *(9)* was performed using an esterification reaction between propionic anhydride and acidified isopropanol (IPA). ARSST tests on that system were performed by heating 6.84 g of propionic anhydride to 118°C and injecting 3.16 g acidified (room temperature) IPA. The injection of the cooler IPA caused an abrupt drop in temperature to about 75°C. Immediately a 250-psig nitrogen backpressure was imposed. Self-heat rate results (Figure 5) are in excellent agreement with the reference data from the Health and Safety Executive (HSE), and are as good or better than results from more expensive calorimeters.

Decomposition of neat DTBP is illustrated in Figure 6. This organic peroxide example demonstrates the ability of the ARSST to handle extremely reactive samples with significant gas generation.

Finally, Figure 7 shows an example of how the Flow Regime Detector (FRED) operates. In this illustration a reactive mixture of BPO (benzoyl peroxide) in styrene monomer was rapidly heated at about 40°C/min. The mixture foamed up at the styrene boiling point, immediately quenching the detector and dropping its temperature (TC2) to that of the boiling liquid. Homogeneous two-phase discharge should be considered when sizing a relief vent for this system.

SUMMARY

The new ARSST adds significant improvements, yet preserves all the important features of the RSST, including the low phi-factor test cell. “Customized” heater calibration provides accurate control over a broad range of temperature ramps. Phase change is easily accommodated. New capabilities include heat-wait-search (HWS) mode and PID control, as well as the latest FAI technology in Flow Regime Detection. Test operation and data reduction are performed in a user-friendly Windows environment. The ARSST retains the low cost and ease-of-use that has made the RSST such a popular and effective laboratory tool.

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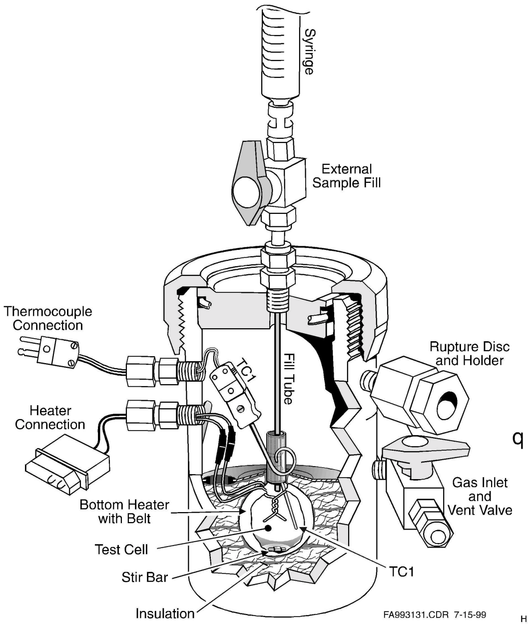

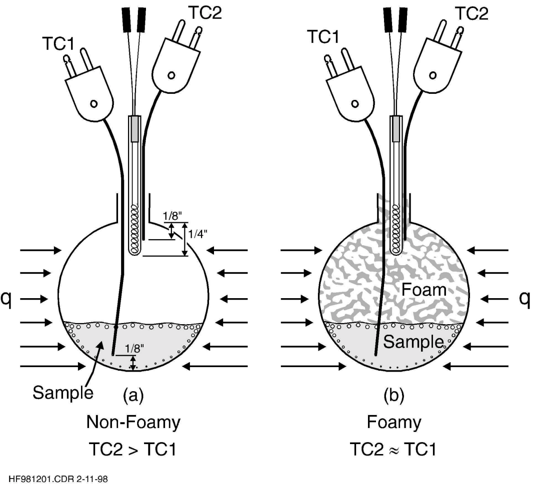

Figure 1 - Schematic of Containment Vessel and Internals.

Figure 2 - Flow Regime Detector.

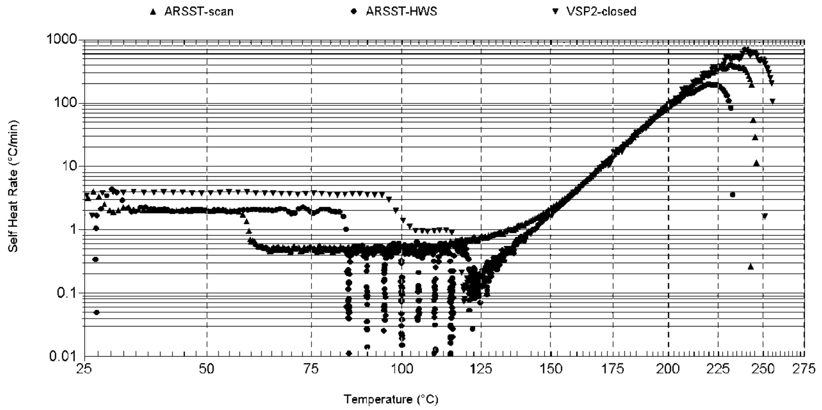

Figure 3 - Self-Heat Rate Data for 25% DTBP in Toluene.

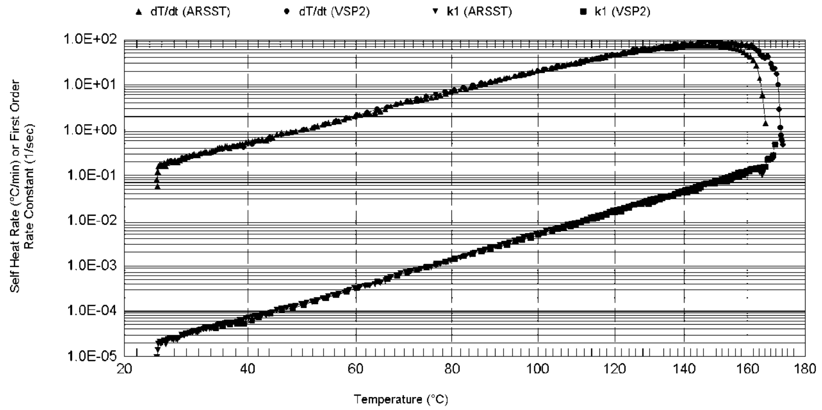

Figure 4 - Self-Heat Rate Data and First-Order Rate Constant for Methanol/Acetic Anhydride.

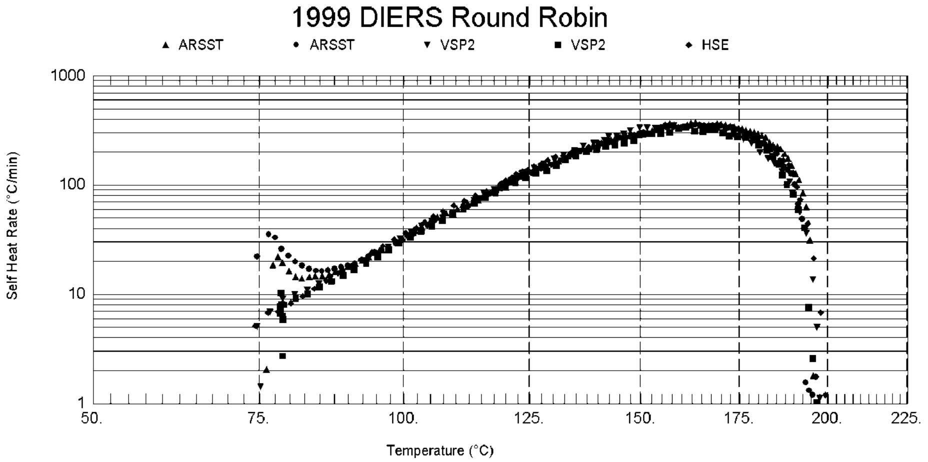

Figure 5 - Composite Self-Heat Rate Plot of Selected Round Robin Data ***(9)*****.**

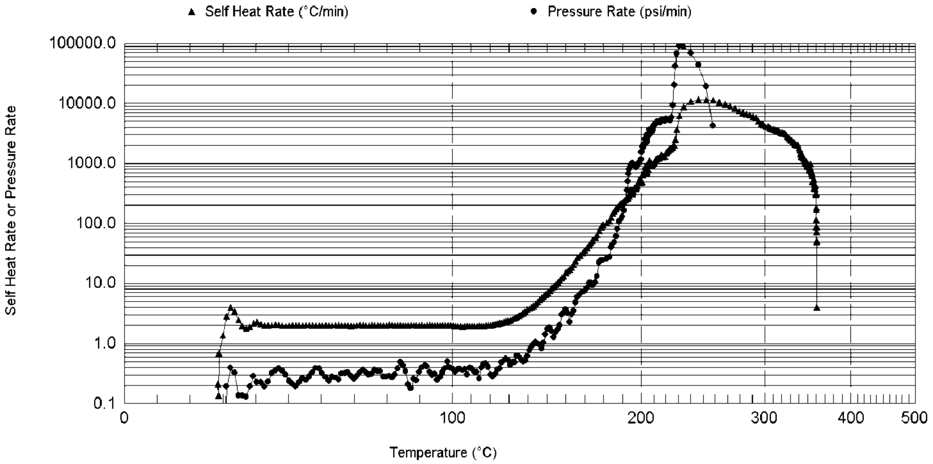

Figure 6 - Self-Heat and Pressure Rate Data for Neat DTBP at 300 psig in the ARSST.

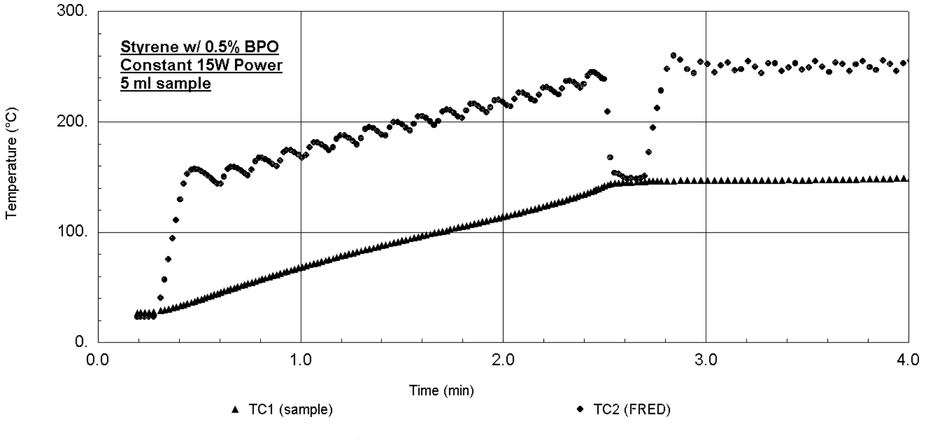

Figure 7 - Example of Flow Regime Detection with the ARSST.