THE VERSATILE VSP2: A TOOL FOR ADIABATIC THERMAL ANALYSIS AND VENT SIZING APPLICATIONS

Charles F. Askonas, Dr. James P. Burelbach, and Dr. Joseph C. Leung
Fauske and Associates, Inc.
16W070 W. 83rd Street
Burr Ridge, Illinois 60521

ABSTRACT

The VSP (Vent Sizing Package) calorimeter was introduced in 1985 as the original DIERS Bench Scale Apparatus for characterizing runaway chemical reactions. Key features include a lightweight (low phi-factor) test cell, adiabatic pressure tracking, and heat-wait-search. The adiabatic operation allows direct application of the temperature and pressure rise rate data to large-scale process vessels. The data are useful for determining the adiabatic heat of reaction, as well as the adiabatic reaction rate used for pressure relief system design. The VSP2 provides automated Windows operation, compactness, and testing flexibility. Features include high pressure injection of reagents, heat removal from the sample during an exotherm using an external cooling coil, and isobaric relief valve simulation. This article summarizes equipment capabilities and presents thermal data for some systems.

INTRODUCTION

The original DIERS Bench Scale Apparatus (also known as the VSP) has been described previously *(1, 2)* and its application to a wide variety of chemical reacting systems has been demonstrated *(3)*. The patented features of a light-weight test cell design along with automatic pressure tracking and adiabatic temperature tracking continually prove it to be a useful tool for measuring temperature and pressure rise rates for thermal analysis and for vent sizing applications. For the latter, the rate of temperature or pressure rise along with the experimental vapor pressure (for a closed system test) provide the needed data. Recently Fauske *(4)* has highlighted these vent sizing features emphasizing the ability to directly scale-up the acquired data to process vessels for the purpose of pressure relief system design. The features and applications of recent improvements to the VSP (hence the name VSP2) are the subject of this paper.

BASIC OPERATING PRINCIPLE

The key features of the VSP2 are illustrated in Figure 1. The low ϕ-factor test cell (typically 35 g) constructed of 304 or 316 stainless steel, Hastelloy C, or Titanium is situated in a 4 liter pressure vessel (~1900 psig rating). Test cells are two inches in diameter with a capacity of 116 m*l*. The test cell contains either a Teflon™ coated or glass encapsulated magnetic stir bar. The apparatus measures sample temperature (T1) and pressure (P1) and external (guard) temperature (T2) and containment vessel pressure (P2). The test cell is enclosed by two heater elements, which are in turn enclosed by thermal insulation material. The purpose

of the inside (test cell) heater is to heat the test sample to a desired temperature. During a search and subsequent runaway period, the test cell heater is turned off and the outside guard heater is regulated to keep an outer aluminum can at the same temperature (T2) as the test cell temperature (T1), thus maintaining adiabatic conditions.

For closed (non-vented) test cells, the pressure in the containment vessel is controlled to balance the test cell pressure. Usually the test cell is allowed to be 20 – 40 psi greater than the containment vessel. This pressure control feature makes possible the utilization of a thin wall test cell design (typically 0.007 inches thick). For open or vented test cells, no pressure regulation is necessary since the vent provides adequate pressure equalization. Tests may be carried out under constant volume (containment volume) or constant pressure or depressurization operation modes. In most open tests, an initial backpressure, usually determined by the desired relief set pressure, is imposed on the system. The containment vessel can be equipped with an external solenoid valve to simulate relief valve operation and maintain constant backpressure.

TEMPERATURE MEASUREMENT

The VSP2 features a single digital multiplexer allowing up to four type K thermocouples to be amplified by a single device (known as the EXP-16) which eliminates uncertainties that exist when two separate, battery-powered amplifiers are used. This multiplexer has on-board cold-junction compensation (based on room temperature). The actual temperatures are furnished to the user by means of a seventh-order polynomial expression which may be calibrated using a TC simulator starting at or below room temperature. Tests can be performed at very cold temperatures by first chilling the VSP2 containment vessel, say in a dry ice/acetone bath.

MAGNETIC STIRRING

A typical test utilizes an off-the-shelf magnetic stirrer plate. However, due to the thickness of the pressure vessel, this stirring is sometimes inadequate for heterogeneous systems consisting of two liquid-phases (such as emulsion polymerizations involving immiscible liquids) or for highly viscous samples. Recently, a strong magnetic "super stirrer" was developed and commercialized by Fauske and Associates, Inc. This stirrer utilizes a neodymium iron boron magnet which provides sufficient magnetic flux through the thick pressure vessel. It also has a built-in tachometer, and the DC motor maintains constant RPM.

The super stirrer gives very good mixing for emulsion polymerizations consisting of an aqueous-phase and an immiscible monomer-phase. Sample data are shown in Figure 2 for the styrene/water system initiated by t-butyl perbenzoate and benzoyl peroxide. It is important to use a baffled test cell with a star-shaped stir bar when testing emulsion polymerizations. Using the super magnet motor drive on an 80-ml sample size and a baffled cell with a star stir bar ensures good mixing of the aqueous- and organic-phases. To confirm that good mixing is actually taking place, thermocouples are placed at different elevations in the test cell. For this test, T1 was positioned 1¼-inches above the base (in what

would be the styrene layer if unstirred) and T3 was placed ¾-inches above the base (in the aqueous layer if unstirred). The fact that both thermocouples agree in Figure 2 indicates that good agitation is occurring throughout the test.

MECHANICAL STIRRING

The mechanical agitation system consists of a small AC motor mounted inside the containment vessel, a specially made test cell, a mechanical linkage, and a motor/shaft assembly mounted inside the 4-liter containment vessel. Special o-rings are packed in the o-ring gland to maintain a pressure seal for closed system tests. Impeller blades may be standard (45° pitch), U-shaped, or otherwise customized. The rotation speed of the motor is typically 300 – 600 rpm. A 100% styrene (thermally initiated) test conducted using mechanical agitation is compared to that with standard magnetic agitation in Figure 3. Notice that the self-heat rate is completely smoothed out using the mechanical agitation.

ISOTHERMAL TEMPERATURE CONTROL (COOLING COIL)

Isothermal operation during an exothermic reaction is readily simulated using a test cell with an external cooling coil. Chilled fluid is circulated through this coil during the isothermal portion of the test (e.g., only the guard heater is on). Subsequently during the thermal runaway portion of the test, the coolant loop is disconnected and the cooling coil is emptied out to minimize its thermal effect.

This method has been used successfully for vinyl chloride suspension polymerization in water. Using the super magnetic stirrer (to thoroughly mix water and vinyl chloride) and two thermocouples in the test cell (to make sure that the sample is well mixed) the data shown in Figures 4 and 5 were obtained. Again a baffled cell with a star-shaped stir bar was used. Thermocouple T1 was positioned 1¼-inches from the base and T3 was placed ¾-inches from the base. In order to simulate plant operating conditions prior to a thermal runaway, the sample was held for 35 minutes at 70°C using a single cooling coil with 10°C water circulating through the 1/16-inch diameter coil. Afterwards, the water was blown out of the cooling coil lines and the sample was allowed to self-heat under adiabatic conditions. The composition of the sample was roughly 50% water containing PVA as a granulating agent, and 50% vinyl chloride monomer, with AIBN (Vazo 64) initiator. The data are in good agreement with a published model.

DUAL CONTAINMENT OPTION

The VSP2 apparatus can be equipped with a second 4-liter quench vessel (Figure 6) to house a catch container containing a quench fluid to halt subsequent thermal runaway of a discharged reacting material, say after a sudden depressurization. The second containment vessel could also simply serve as a gas expansion volume for open system tests to avoid contaminating the insulation, etc. of the primary vessel. The pressure of the quench vessel can be controlled to simulate isobaric conditions, or the quench vessel may simply remain sealed.

SAMPLE CHARGING METHODS

The use of a dedicated 1/16-inch fill line, known as the auxiliary fill line, allows the addition of small quantities of reagents (e.g., adding catalyst(s) at normal reaction temperature) with negligible hold up. This helps to keep the test cell pressure transducer clean of chemicals. The auxiliary fill line and the normal fill line are usually made of 1/16-inch diameter tubing, but 1/8-inch tubing can be used to charge slurries or to handle systems that tend to foam up or otherwise clog a small diameter line. Metered or high-pressure injections can be made via syringe pump or injection piston.

A substance such as chlorine (gas or vapor) may be charged to the test cell directly from a lecture bottle (situated on an electronic balance). If liquid chlorine is being charged, typically the entire test cell and containment vessel assembly is pre-chilled using dry ice or dry ice/acetone. Chlorine (vapor pressure of ~85 psia at room temperature) may then be added either to the vapor or liquid portion (by making the auxiliary fill line a dip-tube) with the addition rate regulated by an appropriate needle valve. The key to using this method is the selection of 1/16-inch diameter Teflon™ tubing (to minimize tension on the balance) between the lecture bottle situated on an electronic balance and the VSP2 containment vessel. A check valve is commonly used to prevent backflow into the lecture bottle. This method of charging works as long as the test cell pressure does not exceed the delivery pressure in the lecture bottle.

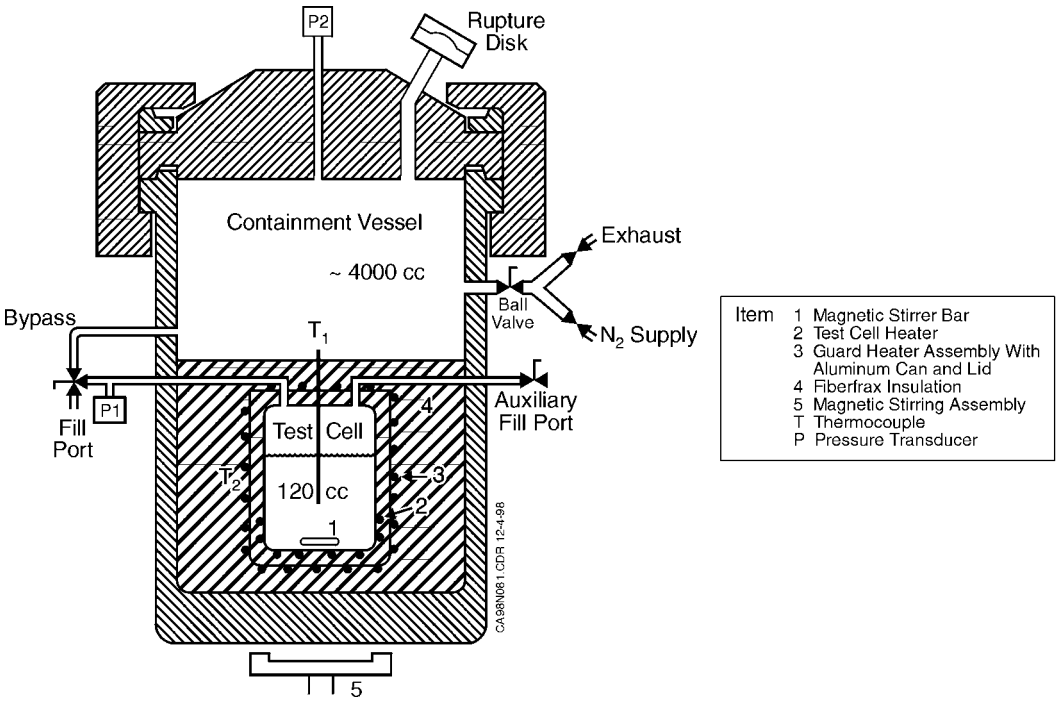

Figure 1 - VSP2 Calorimeter.

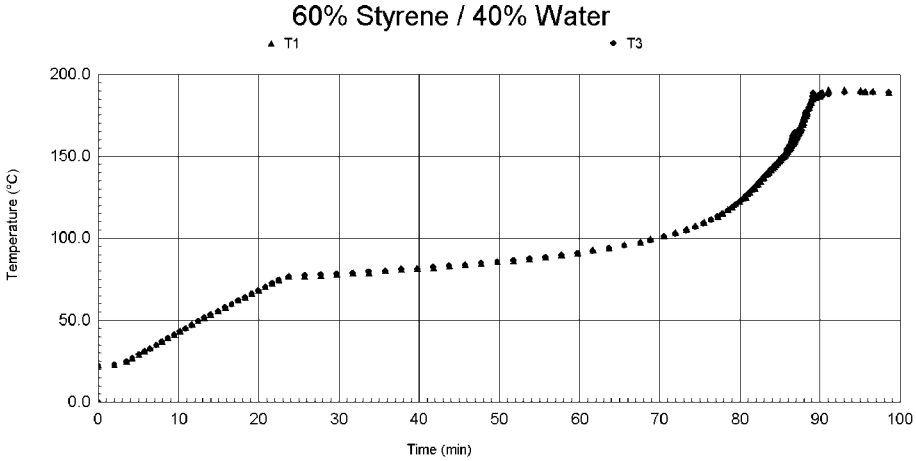

Figure 2 - Temperature Data for Styrene/Water Polymerization.

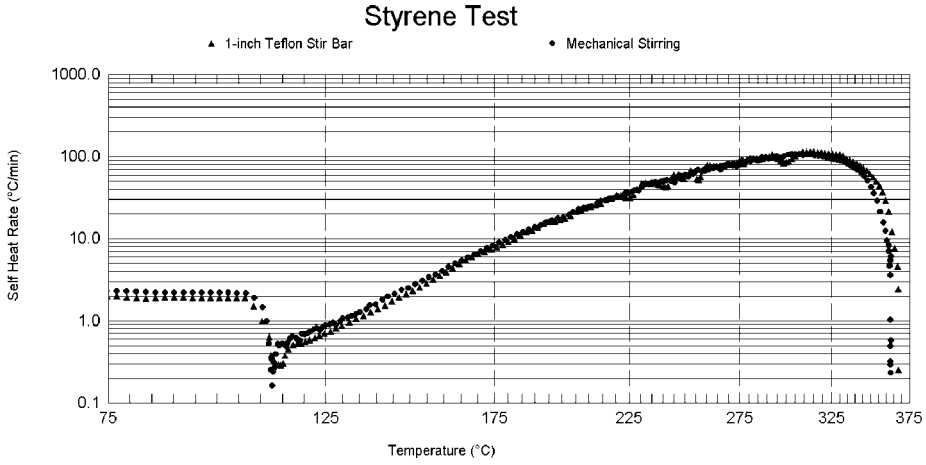

Figure 3 - Styrene Thermal Polymerization.

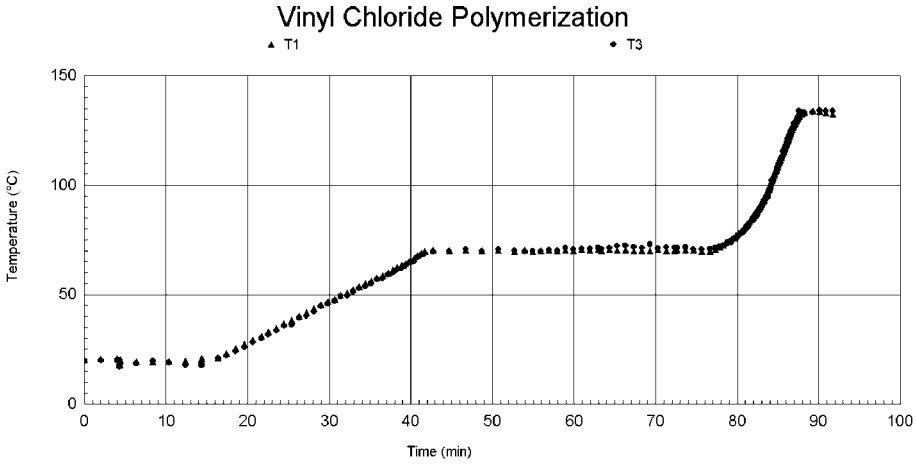

Figure 4 - Temperature Data from Vinyl Chloride Suspension Polymerization.

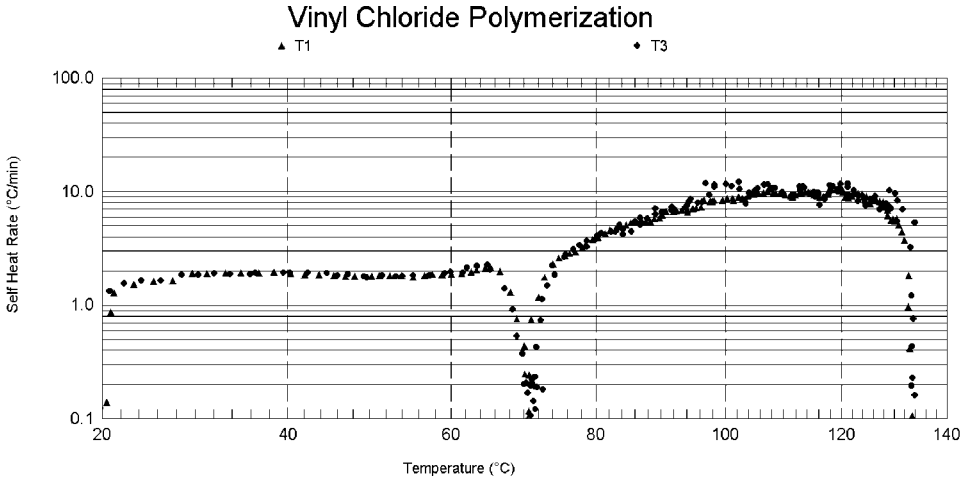

Figure 5 - Self-Heat Rate Data from Vinyl Chloride Suspension Polymerization.

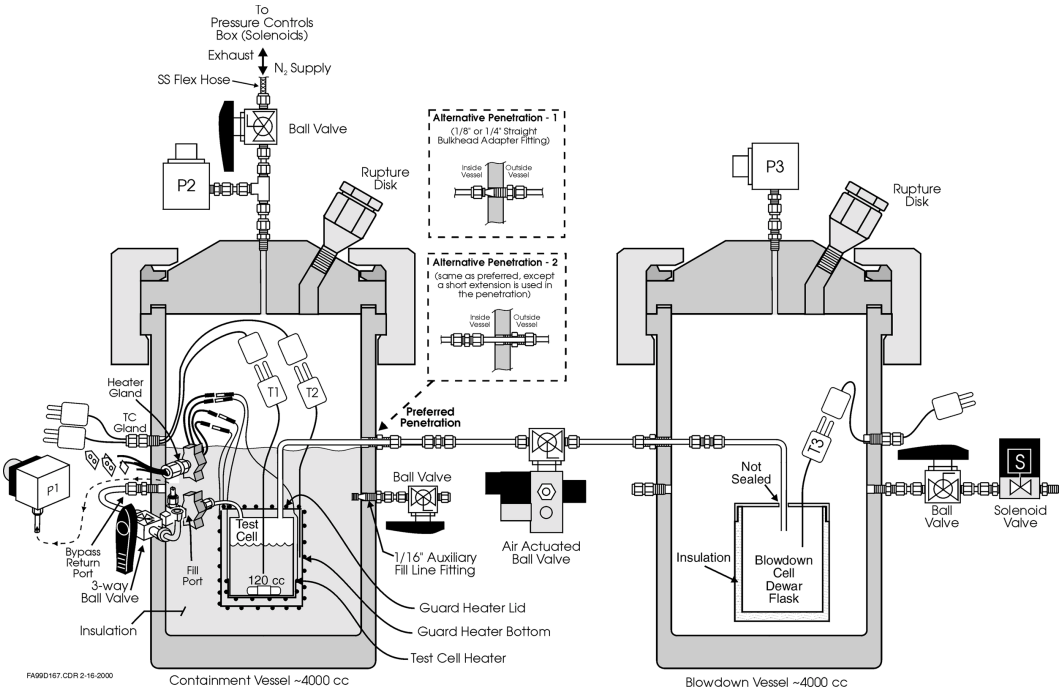

Figure 6 - VSP2 Illustrating Dual Containment Option.

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