

A High Temperature, High Pressure Reaction-Screening Apparatus

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This short note describes an apparatus that has been designed and constructed to allow assessment of the extent of chemical decomposition of fluids and fluid mixtures under high temperature, high pressure conditions. The apparatus is used to screen fluid systems prior to PVT (pressure-volume-temperature) or VLE (vapor-liquid equilibrium) experiments under severe conditions. For a predetermined residence time, the fluids are maintained at the temperature and pressure at which the PVT or VLE experiment will be conducted. The residence time in the reactor is comparable to the expected residence time in the PVT or VLE apparatus. Samples of fluid are withdrawn directly at regular intervals for analysis by gas chromatography, or collected in a sampling vessel for more extensive analysis.

Key words: decomposition; high pressure; high temperature; reactions.

1. Introduction

Recently there has been an increasing amount of interest in obtaining pressure-volume-temperature (PVT) data and vapor-liquid equilibrium (VLE) data for fluids and fluid mixtures at high temperature and high pressure. This is due to the importance of these properties in engineering design and process development [1-5]¹. An inadequate knowledge of these parameters is costly to industry in financial terms [6-12]. Specifically, PVT and VLE measurements are necessary for fluids and fluid mixtures at temperatures greater than 200 °C and pressures greater than 30 MPa, but under these conditions the possibility of decomposition or reaction of the fluids and fluid mixtures is very real. We must therefore con-

sider the thermodynamic, kinetic, and catalytic factors which are involved. Thermodynamic factors include activation energies and equilibrium positions [13]. The primary kinetic consideration is the strong temperature dependence of the rate constant [14]. The construction materials, wetted by the fluids in the experimental measurement apparatus, are often responsible for catalytic effects. Further, since many fluids become highly corrosive under severe conditions, the possibility of damage to instrumentation must also be taken into account.

It is clearly important to assess the possibility and extent of reactions of test fluids in PVT and VLE experiments [3]. Further, it is important to address this issue before the experiments are actually attempted.

The reaction screening apparatus described in this note is a simple apparatus easily constructed from commercially available materials.

2. Apparatus Description

The reaction screening apparatus is shown schematically in figure 1. The heart of the apparatus is a small, thick-walled pressure vessel which serves as the reaction chamber. This vessel was machined from a sec-

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¹Numbers in brackets indicate literature references.

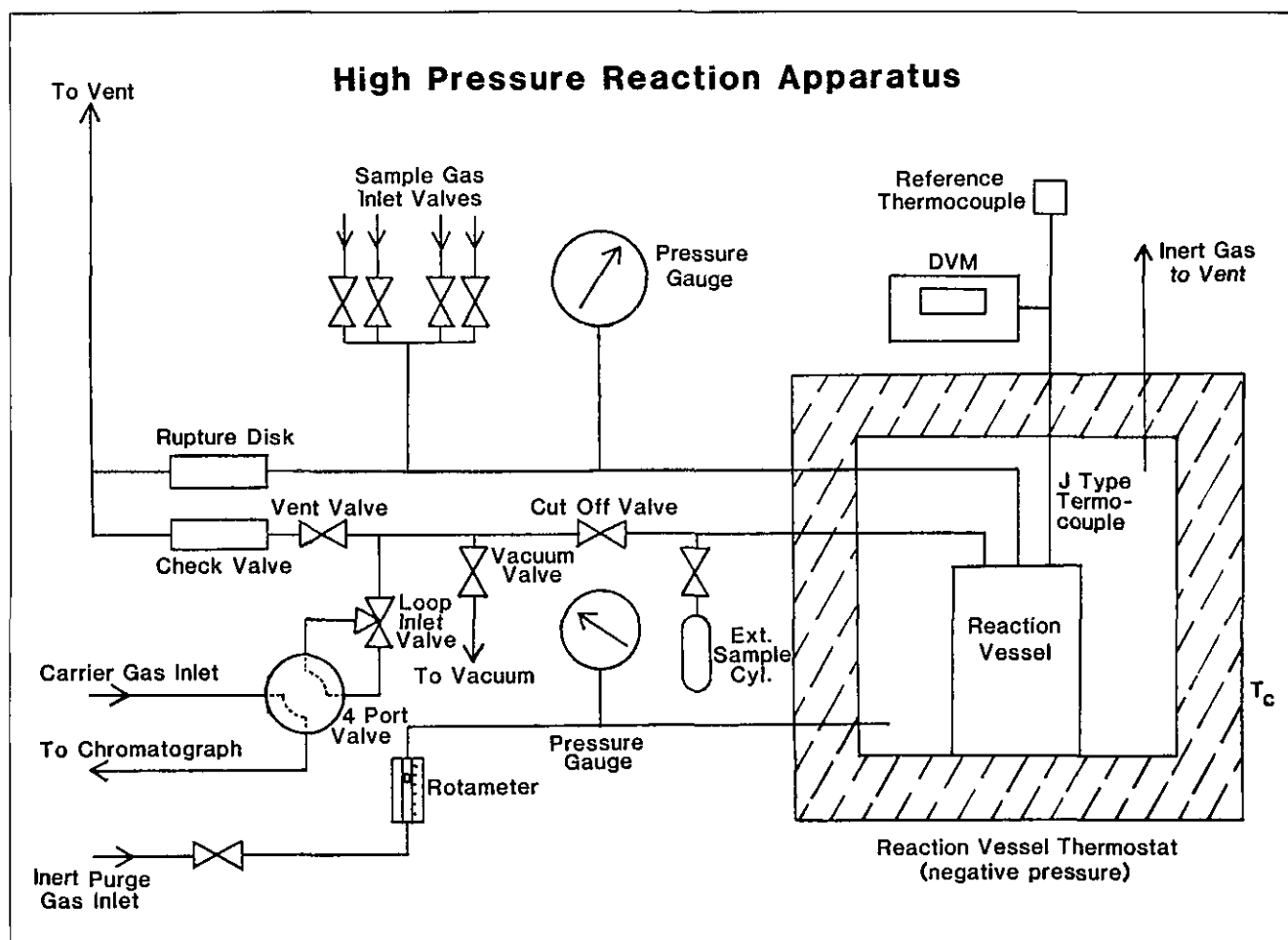


Figure 1—Schematic diagram of the reaction screening apparatus.

tion of work-hardened 316L stainless steel (AISI designation) barstock, and can withstand a pressure of 130 MPa at 250 °C. Tolerances and specifications of this vessel exceed the requirements set forth by the ASME [15]. The cover of the vessel, secured using a bolted closure, contains feedthroughs for introducing the test fluids and removing samples for analysis. Sealing is provided by a gasket of either 316 SS or 25% glass filled PTFE. A thermowell is provided in the vessel to contain a J-type (iron-constantan) thermocouple, the referenced output of which is displayed on a digital voltmeter (DVM in fig. 1).

The pressure vessel rests within an aluminum jacket containing cartridge heaters (not shown in fig. 1). This heating apparatus maintains a constant temperature in the pressure vessel and minimizes temperature gradients.

The pressure vessel, enclosed in the aluminum jacket, is contained in a convection oven (T_c on fig. 1) specifically designed and built for this application. The oven is internally insulated with bonded mineral wool board.

The outer casing of the oven is of welded seam construction with a PTFE gasket providing the door seal. It is maintained at a slight negative pressure by a dedicated blower system, and is equipped with an inert gas purge line. A nondefeatable safety head containing a 68 MPa rupture disk provides over-pressure protection. A combustible gas detector and an electrochemical detector [16] are located nearby to provide additional safety.

Sampling of the contents of the pressure vessel can be done in two ways during the course of a screening test. The sample line is directly connected to a chromatographic four port sampling valve which is in turn connected to an analytical chromatograph. The sampling valve has another three port valve interposed in the sampling loop. This arrangement allows the valve and sample loop to be evacuated before filling, and allows a minimum amount of sample to be expended for each analysis, since the need for purging is minimal.

Alternatively, an external sampling cylinder may be filled with the test fluid and the analysis done off line. This makes possible the use of mass spectrometry and

spectrophotometry, as well as more specific tests.

The apparatus has been used successfully (in conjunction with a direct fugacity measurement system) [17] for over a year. In this application, gaseous mixtures containing hydrogen in binary mixtures with industrially important gases (such as methane, propane, carbon dioxide and carbon monoxide) are tested for reaction with a palladium/silver alloy. This alloy is a construction component of the fugacity apparatus, and under certain conditions of temperature and pressure may act as a catalyst. The reaction screening apparatus has been used to determine the conditions under which decomposition or reaction might occur. The apparatus is also used to determine the effect of test fluids on the palladium/silver component, since many compounds (olefins, organic sulfur compounds, higher hydrocarbons) can damage the alloy under severe conditions.

The reaction screening apparatus is a versatile lab scale semibatch or batch reactor. In it, a variety of fluids and fluid mixtures can be tested with or without catalysts at various temperatures and pressures. Using the reactor in conjunction with the gas chromatograph, reactions, decomposition and nominal rate of reaction data may be obtained.

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