9/12/1995 OSTI

SANDIA REPORT

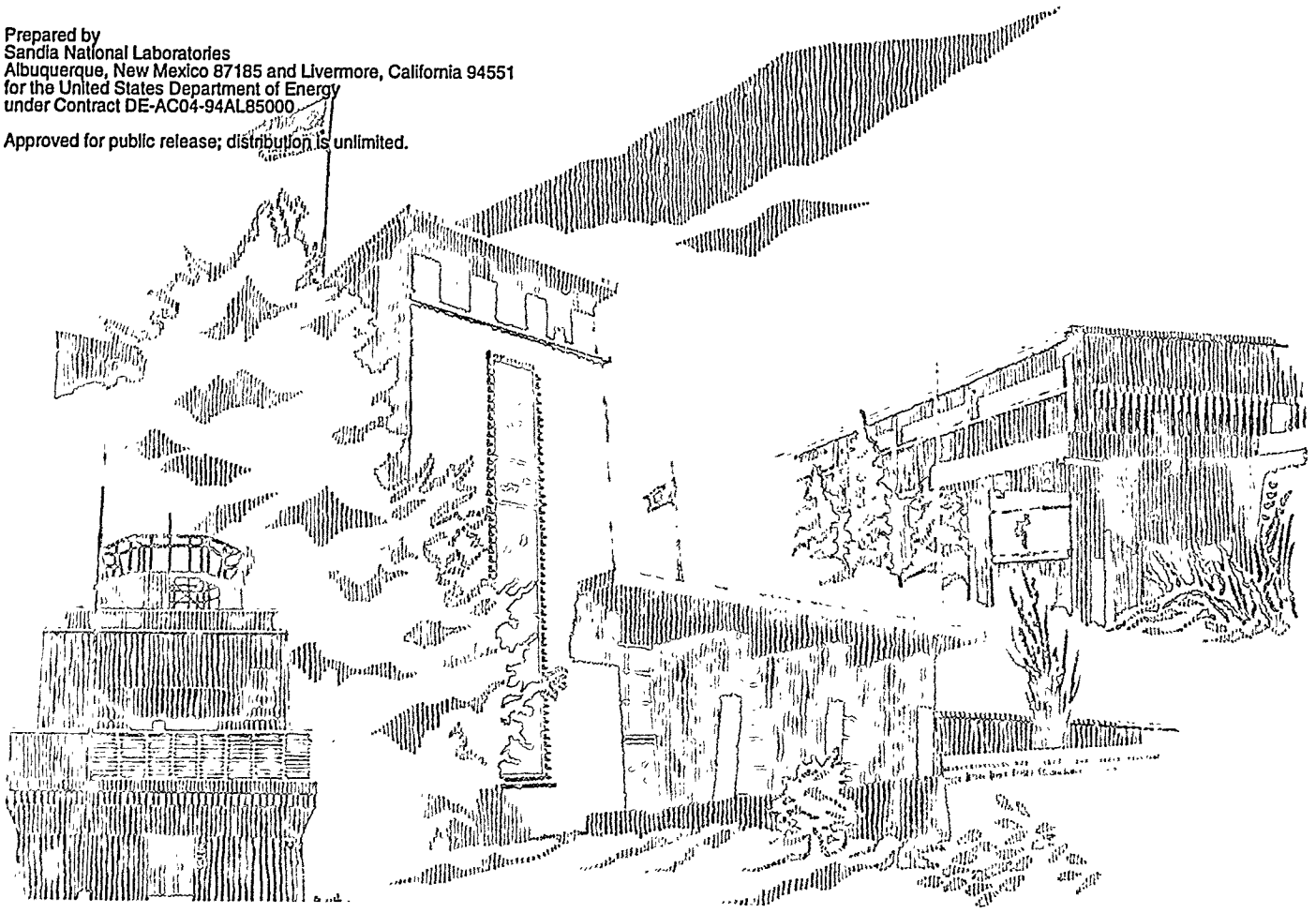
SAND96-8203 • UC–402
Unlimited Release
Printed November 1995

Operation and Performance of the Supercritical Fluids Reactor (SFR)

R.G. Hanush, S.F. Rice, T.B. Hunter, J.D. Aiken

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94551
for the United States Department of Energy
under Contract DE-AC04-94AL85000

Approved for public release; distribution is unlimited.



UC-402

SAND96-8203
Unlimited Release
Printed November 1995

Operation and Performance of the Supercritical Fluids Reactor (SFR)

R. G. Hanush, S. F. Rice, T. B. Hunter, J. D. Aiken

Combustion Research Facility
Sandia National Laboratories
Livermore, CA 94551-0969

ABSTRACT

The Supercritical Fluids Reactor (SFR) at Sandia National Laboratories, CA has been developed to examine and solve engineering, process, and fundamental chemistry issues regarding the development of supercritical water oxidation (SCWO). This report details the experimental apparatus, procedures, analytical methods used in these experiments, and performance characteristics of the reactor. The apparatus consists of pressurization, feed, preheat, reactor, cool down, and separation subsystems with ancillary control and data acquisition hardware and software. Its operating range is from 375 - 650 °C at 3250 - 6300 psi with residence times from 0.09 to 250 seconds. Procedures required for experimental operations are described. They include maintenance procedures conducted between experiments, optical alignment for acquisition of spectroscopic data, setup of the experiment, reactor start up, experimental operations, and shutdown of the apparatus. Analytical methods used are Total Organic Carbon analysis, Gas Chromatography, ion probes, pH probes, turbidity measurements and in situ Raman spectroscopy. Experiments conducted that verify the accuracy of measurement and sampling methods are described.

INTRODUCTION

Supercritical water oxidation (SCWO) is a hazardous waste treatment process which is being developed as an alternative to other methods of waste disposal such as incineration, bioremediation, and interment. Organic waste in aqueous solution or slurry is pressurized and heated above the critical point of water (374 °C, 3250 psi), and at these conditions, organic compounds are easily oxidized to form less hazardous materials. Ideally, the final products produced by the SCWO process are carbon dioxide, molecular nitrogen, and water. All releases of effluent can be contained and monitored prior to release. SCWO is applicable to a wide range of waste streams, including energetic materials such as explosives, biological, toxic, and chemical/radiological mixed wastes, as well as industrial waste water. It is energy efficient; the process occurs at much lower temperatures than incineration, and energy from the combustion of wastes can be used for cogeneration of the process. The relatively low temperatures required for highly efficient destruction of the waste also prevent the formation of NO_X, a prime concern in higher temperature waste treatment methods.

In comparison, incineration has the disadvantages of potential uncontrolled release of waste products and higher expense. Bioremediation, while efficient and cost effective, has excessively long batch cycles (i.e. 30 days), and handles only relatively low concentrations. Interment ignores the real issue of treatment and disposal, leaving the problem for the future.

The Supercritical Fluids Reactor(SFR), shown in Figure 1, has been developed to examine and solve technical issues associated with the development of the SCWO process. Examination of applied engineering design concerns, destruction methods and efficiencies, and effluent composition and treatment is necessary to improve the process for commercial feasibility. Fundamental analyses of the chemical kinetics involved are undertaken to expand our knowledge of the chemistry occurring during the oxidation reactions and to allow the development of models intended to aid in engineering design.

This report is a detailed description of the SFR and the procedures associated with collection and analysis of results from a variety of experimental methods. Equipment used for experimental operations is discussed first, in two parts; a description of the apparatus, followed by a description of the control and data acquisition hardware. Procedures necessary for operation and data acquisition are detailed in sections on maintenance, optical alignment, setup of the apparatus and peripheral hardware, reactor start up, experimental procedures, and shutdown of the apparatus and peripheral hardware. Materials tested in this reactor, and the analytical methods used, are discussed in the following section. The final section of this report outlines experiments that have been performed, and the conclusions drawn, from the data collected on the performance of the experimental apparatus.

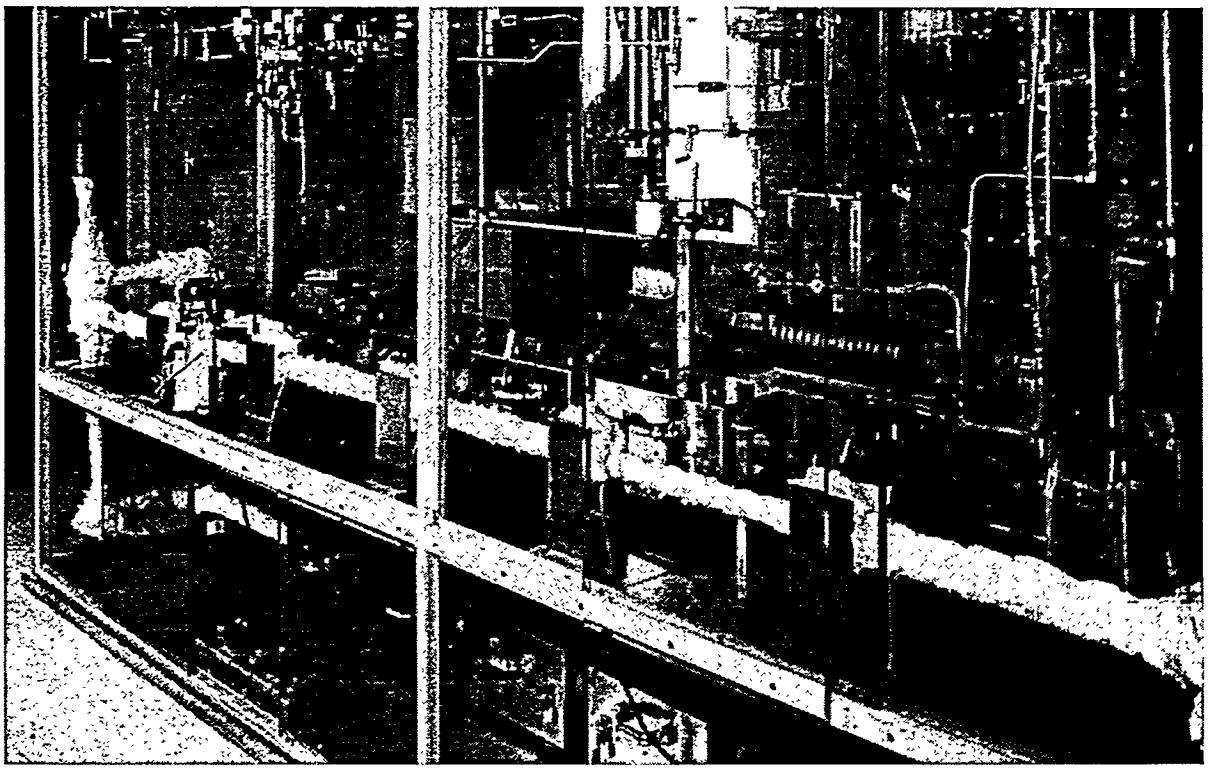


Figure 1. Photograph of the Supercritical Fluids Reactor.

EQUIPMENT

The SFR is used to conduct experiments at temperatures and pressures above the critical point of water. It consists of 7 operational subsystems (pressurization, feed, two parallel preheat subsystems, reactor, cool down, and separation) and is shown schematically in Figure 2; detailed schematics are included in Appendix A. Control and data acquisition hardware and software are also an integral part of the entire reactor system. These subsystems provide an overall reactor that is capable of a wide range of experimental parameters and configurations.

Flow of the experimental feeds begins in the feed subsystem where low pressure for supply to the high-pressure pumps is generated. The low pressure feeds flow to the two parallel preheat subsystems for pressurization and heating. After pressurization, the flows can be diverted to a single preheat line and mixed prior to heating, or preheated separately and mixed at experimental conditions. Flow continues through the reactor subsystem, which is kept at isothermal conditions during the reaction. This section allows optical accessibility to the reacting flow. Upon exiting the reactor subsystem, the flow is cooled to ambient temperature in the cool down subsystem. The separation subsystem then separates any solids produced during the process, from the liquid and gaseous components of the flow stream. After separation, each component may be collected for analysis and later disposal.

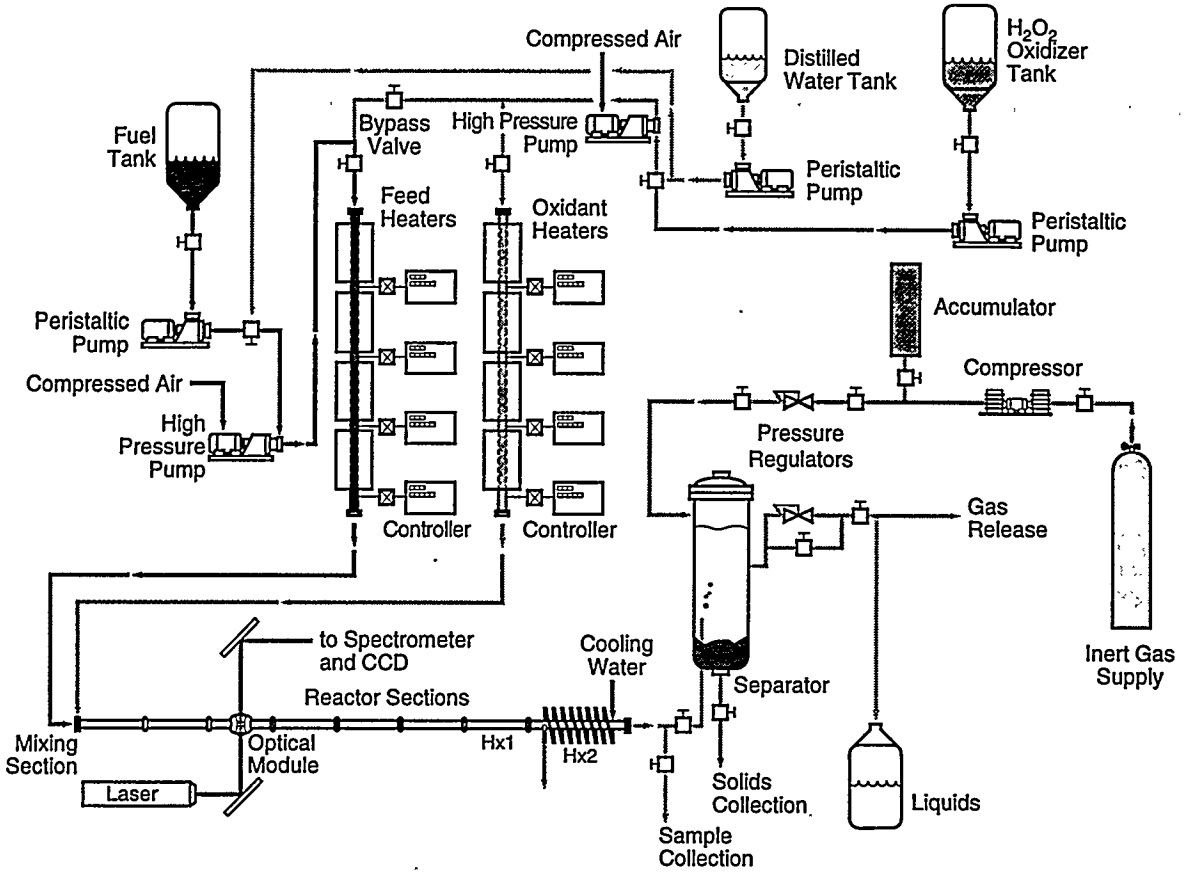


Figure 2. Schematic diagram of the Supercritical Fluids Reactor.

The system is rated for experimental operation at temperatures as high as 650 °C and at pressures up to 6300 psi. As a safety measure, the reactor is housed in an enclosure measuring four meters long, one meter wide, and two meters high, with walls constructed of removable transparent Lexgard panels, allowing easy viewing of the reactor in operation. The reactor system has a total volume of 1228 cm^3. Feed materials are inert gases, water, hydrogen peroxide (used as an oxidizer), and the general classification referred to as fuels throughout this report. Specifically, fuels used are: surrogate waste streams designed to duplicate production processes, inorganic salts in aqueous solution for determination of salt deposition rates, and carbon based solvents of interest as waste stream components and/or additives. Maximum feed concentrations are 30 wt% hydrogen peroxide in water and 10 wt% fuels in water. Mass flow rates through the reactor ranging from 0.17 to 2.0 gm/s are achievable with total residence times of 2.2 to 250 s. Optical experiments may be conducted with residence times ranging from 0.09 to 81.2 s for oxidation experiments.

Pressurization Subsystem

The pressurization subsystem consists of an inert (buffer) gas supply, a compressor, an accumulator, and associated regulator and flow hardware located outside the reactor enclosure. The buffer-gas is used in the separation subsystem to dilute excess oxygen from the oxidation process, and to aid in pressure control of the reactor. Argon is the gas of choice, to simplify the measurement of gaseous effluent composition. Buffer-gas pressure is intensified to 8000 psi by a Haskel AG-152, air powered, positive displacement compressor which supplies a Hydropac PV45-01-19SE, 250 cm^3 accumulator. It is delivered to the reactor through 16.8 meters of 6.4-mm (1/4 in) outside diameter (OD), 1.8-mm (0.07 in) inside diameter (ID), stainless steel tubing. Buffer-gas pressure into the reactor is controlled by a Tescom 26-1021, 10,000 psi pressure regulator.

Feed Subsystem

Water, oxidizer, and fuel mixtures are stored in three separate one gallon reservoirs in the feed subsystem. A gravity feed, through flexible tubing of various compositions, dependent on feed compatibility, is used to deliver the feeds to Masterflex 7520-00 peristaltic pumps. These pumps provide a constant head pressure of 20 psi to the preheat subsystems. Three-way valves are provided between pairs of reservoirs for easy switching from water to fuel, and oxidizer.

Preheat Subsystems

The two parallel preheat subsystems pressurize and heat the fuel and oxidizer to operating conditions. In each subsystem, an Autoclave Engineers PPSF 111, high-pressure, positive displacement pump with a working volume of 0.845 cm^3 pressurizes the feed at the rate determined (in cycles per minute) for the desired experimental conditions. A manual bypass valve (Autoclave Engineers 60VM4071) is installed between the two parallel systems to provide for 'single' or 'dual' line modes of operation. During single line operation pressurized flow from one line is diverted through the open bypass valve from one preheat system into the parallel system prior to heating. Closing this bypass valve maintains separation of the feeds through the preheaters for dual line operation. Feeds are supplied to the preheaters through 2.9 meters of 6.4-mm (1/4 in) OD, 1.8-mm (0.07 in) ID stainless steel tubing. A coiled length of this tubing leads into each set of preheaters to accommodate thermal expansion of the reactor. The volume between the pumps and preheaters is 7.4 cm^3 in each line.

Feed flows are preheated through 3.1 meters of 14.3-mm (9/16 in) OD, 4.8-mm (3/16 in) ID , Inconel 625 tubing. Six heated pieces of tubing are connected by Autoclave Engineers, 9/16-in, Inconel 625 tees equipped with a Type K thermocouple inserted into the centerline of the flow. Heat is delivered in the first four stages by Marshall 2001, 875 W, radiative furnaces. The final two stages are heated by Watlow 125CH47A3X, 375 W, resistive cable heaters. Each of the cable heaters are insulated with two layers of 1/2-in thick Fiberfrax Durablanket-S, 8 lb/ft^3

insulation. The internal volume through the preheaters is 56.1 cm^3 in each line.

When operated with the flows heated separately, mixing occurs in an Autoclave Engineers, 9/16-in, Inconel 625 cross, illustrated in Figure 3, equipped with a Type K thermocouple inserted into the centerline of the flow. The opposing flows are mixed under turbulent conditions by combining the flows at a 180° angle of incidence. After mixing, flow into the reactor is orthogonal to the opposing streams.

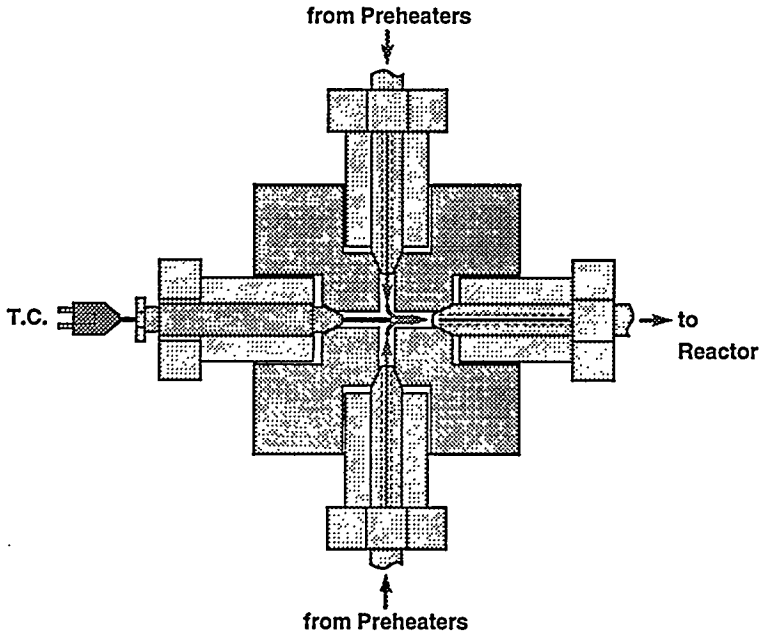


Figure 3. Diagram of the SFR mixing cross. Opposing flows meet at 180° angle of incidence, are mixed and exit orthoganolly into the reactor. Temperature is monitored at the point where mixing occurs.

Reactor Subsystem

The reactor subsystem consists of six sections of 14.3-mm (9/16 in) OD, 4.8-mm (3/16 in) ID, Inconel 625 tubing. Each section is 0.61 meters long and heated by one Watlow 125CH47A3X, 375 W, resistive cable heater. A convection cooler, using compressed air flow controlled by a Nupro series 'M' metering valve, is installed on each section, as necessary, to remove excessive heat released from oxidation reactions. Each section is insulated with two layers of the Fiberfrax insulation. The sections are joined together by Autoclave Engineers, 9/16-in, Inconel 625 tees equipped with a Type K thermocouple inserted into the centerline of the flow. The entire reactor subsystem, including the tees, is 3.8 meters long, and has a volume of 68.6 cm^3.

An optical cell constructed of Inconel 625, illustrated in Figure 4, provides direct optical access to the reacting flow. Three ports, 2.0-mm in diameter, at 90° intervals are fitted with Hemex CSI ultra VUV grade sapphire windows procured from Crystal Systems Inc., and manufactured per Sandia drawing number A53648. The optical cell can be inserted at any point in the reactor subsystem, allowing optical access to the flow over a wide range of residence times. The cell is heated by 2 Watlow STB2J1J11, 175 W, resistive, band heaters. Three layers of the Fiberfrax insulation, with cutouts for optical access, are used to prevent excessive heat losses from the optical cell. Misalignment of the cell, due to thermal expansion of the reactor during high temperature operation, is reduced by mounting the cell in a stainless steel stand which is in turn mounted to the reactor enclosure, centering the expansion of the reactor around the cell.

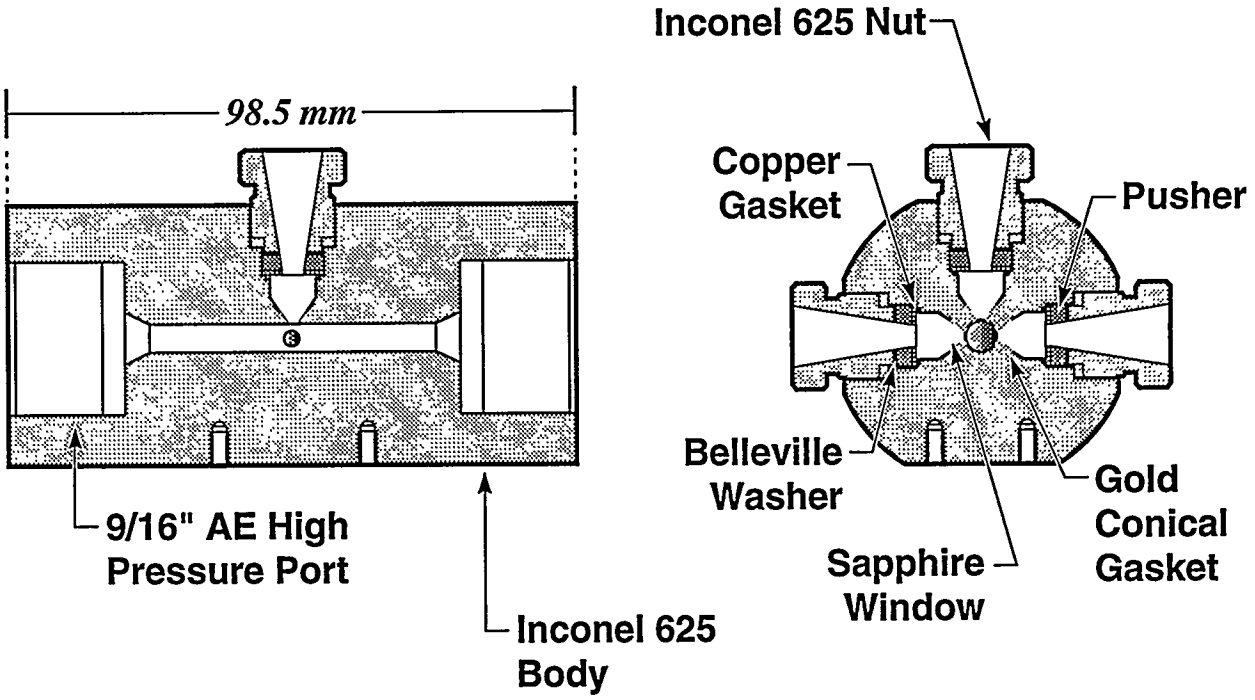


Figure 4. The Optical Flow Cell. Three ports at 90° intervals allow the flow to be directly probed by a laser, and optical data collected.

The design of the cell relies on a balance between the force exerted on the window by the pressure within the cell and the force applied to the window by the nut and the pusher. The Belleville washer serves as a spring that maintains sufficient force on the windows as the cell size changes relative to the window, with temperature. The coefficient of thermal expansion, μ, is 1.3 μm/m-°C for the cell (Inconel 625) and 7.7 μm/m-°C for the sapphire window, $\Delta\mu = 5.3 \times 10^{-6}$. The length (l) of the window is 1.7 cm (0.44 in). At 525 °C, (ΔT = 500 °C) the change in length between the position of the pusher set at ambient temperature and the sealing point of the sapphire to the cell

is simply $(\Delta\mu)(\Delta T)l$ = 0.003 cm (0.0012 in). To maintain compression on the gold seal, the Belleville washer must provide travel of 0.003 cm and sufficient force to offset the force on the window from the high pressure fluid inside the cell.

The force constant, k_w, of the washers used in the design is approximately 1.4 x10^7 N/m (80,000 lb/in), such that at full compression the washer displacement, d(max) = 0.013 cm (0.005 in), resulting in a force on the washer of F_w(max) = 1780 N (400 lb). When the cell is heated, the washer displacement changes 0.003 cm such that d = 0.010 cm corresponding to F_w =1400 N. The force on the window from the fluid is simply $F_f = PA$, where P is the pressure in the cell and A is the effective area of the window that is before the seal. If the seal is estimated to be located halfway up the tapered side of the window, A=0.383 cm and F_f = 1050 N. The opposing value of 1400 N is too close within the estimates in this calculation to use such a design. However, by placing three washers together such that the concave surfaces are all oriented toward the window, the effective force constant of the system can be increased in an additive fashion, such that the k_w for three washers is 4.2 N/m. With this design, at full compression, d(max) = 0.013 cm, F_w(max) =5300 N (1200 lb), and F_w at temperature is 3150 N.

In practice, F_w is not measured. The washers are compressed by the nut that is driven by a torque wrench such that F_w=T/KD, where T is the torque value, K is a thread constant (taken to be 0.2 for unlubricated threads), and D is the thread diameter of 1.75 cm (11/16 in). The torque on the wrench is calculated to be 168 in-lb (19 N-m), which is very near the measured 175 in-lb, where the feeling on the wrench is that of significant stiffening or "bottoming out". At this point the three washers are flat and adequate force is applied to the gold gasket to deform it into a good seal.

After approximately 20 thermal cycles the windows eventually begin to leak and the ambient temperature torque on the windows has dropped to below 100 in-lb. This is probably due to creep of the gold gasket allowing the window to sink deeper in the seat. As the gasket thins, compression on the washers is relieved and d and F_w decrease. At a point corresponding to about 0.010 cm change in the thickness of the gold gasket, which was originally 0.025 cm, F_w at experimental temperatures cannot offset the force of the fluid. To repair this problem the windows are re-tightened to 175 in-lb. Note that a translation of 0.010 cm corresponds to lowering the torque to about 75 in-lb (at 25 °C), which is typical of the torque observed on poorly sealed windows.

Cool Down Subsystem

The effluent is cooled to ambient temperature in two stages upon exiting the reactor subsystem. An uninsulated length (0.84 meters) of 14.3-mm (9/16 in) OD, 4.8-mm (3/16 in) ID, Inconel 625 tubing is used as a convection heat exchanger. Effluent enters this heat exchanger at operational temperature and exits at subcritical temperatures. A Parker DHTC-IN-4, water cooled, coiled, counterflow heat exchanger, 5.9 meters long with an ID of 3.8-mm (0.148 in) reduces the fluid temperature to ambient.

Separation Subsystem

The resulting three-phase effluent, composed of the liquid and gaseous effluents combined with any inorganic solids, which precipitate out of the waste, flows through 1.9 meters of 6.4-mm (1/4 in) OD, 1.8-mm (0.07 in) ID, stainless steel tubing and is separated in a 650 cm^3 Autoclave Engineers 401A-5799 gravity separator vessel. From the separator, 1.2 meters of 6.4-mm (1/4 in) OD, 1.8-mm (0.07 in) ID, stainless steel tubing transport the gaseous and liquid effluents to a Tescom 26-1721, 6,000 psi backpressure regulator in parallel with an Autoclave Engineers 30VM-4071-OM, 60,000 psi, Inconel 625 metering valve. Liquids and gases flow together to a single collection vessel, where liquid effluent is collected for analysis and/or disposal, and gaseous effluent is vented to the atmosphere. The buffer-gas from the pressurization system maintains an adequate gas head in the separator to dampen the large pressure fluctuations inherent in the release of high-pressure liquids from the separator through the backpressure regulator/metering valve assembly.

Control and Data Acquisition

Reactor control and data acquisition are accomplished through a combination of valves, electronics, and computers. Manually actuated, air operated (AO), normally closed valves are installed in the pressurization subsystem and in the reactor enclosure. All AO valves are actuated from the System Control Panel shown in Figure 5. In the pressurization subsystem, valves are installed between the buffer-gas supply and the compressor (valve C2), at the accumulator (C5), between the compressor and the inlet regulator (C6), and between the inlet regulator and the reactor enclosure (C8). Pneumatic drive pressure to the compressor is actuated by switch C3. In the reactor enclosure, valves are installed on each preheat line between the high-pressure pumps and the preheaters (valves S1 and S2), between the counterflow heat exchanger and the separator (S8), and between the parallel backpressure regulator/metering valve assembly and the effluent collection (S6). One normally open AO valve (S5) is installed between the separator and an emergency vent line for emergency depressurization.

One normally closed solenoid valve is installed on each high-pressure pump (to allow compressed air flow to be shut off) and controlled from the System Control Panel. Switch S10 actuates the valve on the fuel line high-pressure pump (HP1) and S11 actuates the valve on the oxidizer line high-pressure pump (HP2). A Nupro series 'M' metering valve is used to meter compressed air flow to each high-pressure pump; flow rate through the reactor is a function of air flow to the pumps.

Type K thermocouples, with a 0.062-in Inconel 600 ungrounded sheath, are installed throughout the reactor to monitor fluid and tubing skin temperatures. Skin temperatures are measured by clamping a thermocouple to the center of each piece of heated tubing. Fluid temperatures are measured by inserting the thermocouple through a custom high-pressure feedthrough allowing fluid temperatures to be measured at the centerline of the flow.

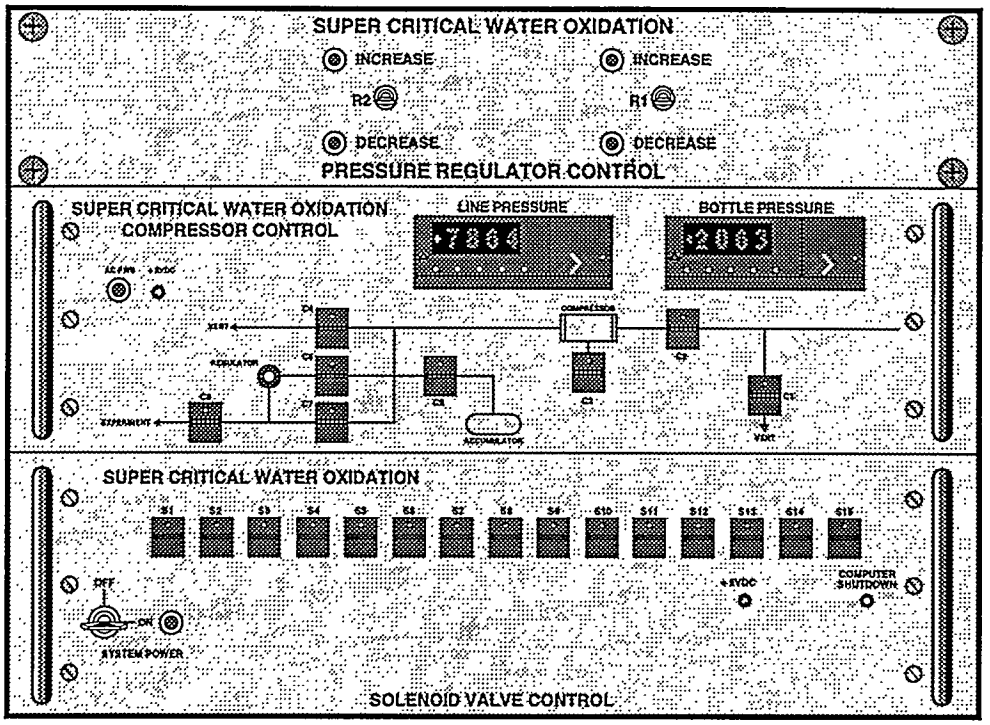


Figure 5. The System Control Panel for the SFR. Control of pressure regulation, the pressurization subsystem, and the reactor air operated valves is accomplished from this control panel.

Omega 6070A temperature controllers monitor the fluid temperatures in the preheat sections and control power to the preheaters. Tube skin temperatures in the preheaters are monitored by Omega CN5000 temperature controllers to ensure the tubing remains within its safe operating range. Should the safe operating temperature of the pressurized tubing be exceeded, power to the associated preheater is temporarily interrupted. Fluid temperatures in the reactor subsystem are monitored and controlled by Watlow 945 temperature controllers which cycle power to the heaters to maintain isothermal conditions throughout the reaction zone. Protection of the reactor subsystem against over heating is achieved by computer control discussed later in this section.

Pressure is monitored at four locations in the reactor, and controlled by both the backpressure regulator in the separation subsystem and the inlet regulator in the pressurization subsystem. A Teledyne Taber 2205 pressure transducer is installed in each of the preheat systems between the high-pressure pump and the AO valve which controls flow into the preheaters. Another Teledyne Taber 2205 pressure transducer, located between the reactor subsystem and the valve controlling flow into the separator, measures reaction pressure which is monitored on a Daytronics 3270 strain gauge conditioner/indicator. Separator pressure is monitored by a Paroscientific 410K-101 transducer installed in parallel to the backpressure regulator/metering valve assembly. Control of the regulators is accomplished from the System Control Panel with the Pressure Regulator Controls. The backpressure regulator is controlled by switch R1 and the inlet regulator is controlled by switch R2.

All temperature and pressure data are transmitted to an Omega OM-900 Data Acquisition and Multiplexer System for computer control and data acquisition. Temperature and pressure data are monitored and recorded every eight seconds on an IBM, 25 MHz, 386 PC using a custom C+ program entitled 'SFR'. Fluid temperature setpoints for the preheaters and reactor are controlled from this program. Reactor subsystem overtemperature control is also performed by this program; should an overtemperature condition be detected, the appropriate heater is de-energized by 'SFR'.

Optical data are acquired using a Coherent Innova 70 argon ion laser delivering 2W at 514.5 nm to perform Raman spectroscopy. The Raman signal is delivered through an optical system to a Spex 1870B, 0.5 meter focal length spectrometer equipped with a 2400 rule/mm grating. The spectrometer is coupled to a Photometrics CH220 camera head with a Thomson CSF TH7882 CDA 384x576 pixel CCD array to yield a dispersion of approximately 0.1 Å/pixel. The time-integrated signal is handled by a Photometrics CC200 camera controller. A custom LabView version 2.2 program, 'CCD Control', running on a Macintosh IIfx, interfaces the user to the CCD camera and its control electronics in the optical system. Parameters such as exposure time, signal averaging, and background subtraction are controlled and spectra may be recorded and stored for further analysis.

PROCEDURES

Procedures for conducting experiments in the SFR are divided into six categories: maintenance, optical alignment, setup, reactor start up, experimental, and shutdown. Maintenance activities are those performed between experiments to maintain the reactor in operating condition. Optical alignment procedures must be completed when acquisition of spectroscopic data is desired. Setup operations involve definition and preparation of a specific experiment. Reactor start up procedures establish operational pressure and temperature conditions in the reactor. Experimental activities are carried out for collection of experimental data. Shutdown procedures are followed at the end of an experiment to de-energize the equipment.

Maintenance

Assembly and disassembly of the high-pressure fittings in the SFR are to be done only by authorized high-pressure installation personnel in accordance with the Sandia National Laboratories Pressure Safety Manual (1995). All high-pressure fittings are from Autoclave Engineers, and rated at 60,000 psi at ambient temperature. Both 1/4-in and 9/16-in sizes are used in the SFR. All heated fittings are 9/16-in and fabricated from Inconel 625. Upon any disassembly a visual check is required to inspect for wear and/or damage of the tubing and fittings. Removal of some insulation may be necessary for disassembly, however, insulation removal should be kept to a practical minimum. Prior to assembly, all fittings which will be exposed to heating must be lubricated with Fel-Pro C5-A lubricant to prevent seizing of the threads. All fittings are assembled finger tight and then torqued 1/8 of a turn to seal.

On occasion, the reactor requires cleaning due to the use of unusual process chemicals during SCWO experiments. The 9/16-in tubing may be reamed out on an 'as needed' basis, and all 1/4-in tubing is discarded whenever necessary. Each piece of tubing is disassembled from the reactor and honed with a 0.20-in diameter metal brush to clear out residual chemicals and corrosion. The tubing interior is then rinsed with water and reinstalled.

Material deposits, pitting, and breakage of the optical cell windows, as indicated by reduced transmittance of the aligned laser through the cell (optical alignment is discussed in the following section), requires removal and cleaning or replacement of the windows. Removal of the optical cell windows entails removal of the optical cell and disassembly of the sealing assembly to expose the window. Soft padding is inserted between the window and the sealing nut, which is then hand tightened. Hydraulic pressurization of the cell ejects the window from the sealing washer, after which the window can be removed. Internal window surfaces are polished with 10 and 3-micron polishing paper in respective order, and reinstalled in a vertical attitude to avoid uneven loading. The sealing assembly is then installed, threads are lubricated with Fel-Pro C5-A lubricant and torqued to a maximum of 175 in/lbs.

For experiments requiring dual-line operation, the parallel preheat subsystems are assembled to the reactor subsystem at the mixing cross. For single-line operation the preheat subsystem not in use is isolated from the rest of the reactor. This is accomplished by removing the appropriate fitting leading into the mixing cross and plugging the exposed port of the cross with a high-pressure plug. The manual bypass valve installed prior to the preheaters should be opened at this point to avoid possible rupture of the burst disk protecting the preheat line whose AO valve will remain closed for single line operation. Conversion from single line to dual line operation is the inverse of this procedure.

Fluid leaks from the weep holes provided in the valve body of the high-pressure pumps indicate servicing of the hydraulic valve body is necessary. Removal of the pumps requires that both low and high-pressure feed lines be removed as well as the compressed air line. The entire pump is then removed with the mounting bracket as a unit by removing the two 1/4-in allen head screws at the base of the mounting bracket. The four 10-mm nuts at the base of the pneumatic assembly are removed allowing the valve body and lower pneumatic section to be separated from the rest of the pump as an assembly. A thin wall (1-3/4-in OD) 37-mm socket is used to remove the cap nut which retains the sealing assembly. Both inlet, and outlet check valves are removed for inspection; damaged or worn parts are replaced from Autoclave Engineers rebuild kit M-0226. The sealing assembly is then carefully driven out with a 3/32-in punch, with access from the inlet port of the valve body. The sealing assembly seals are removed and discarded. Using the parts provided in Autoclave engineers' rebuild kit M-0143, all sealing assembly seals are lubricated with Kluber Lubrication's Isoflex Topas NB 52 and replaced. Prior to assembly all parts are cleaned and lubricated with Topas NB 52 lubricant. Installation is in the reverse order of the disassembly procedure with the only torque specification being 65 in/lbs at the four 10-mm nuts on the pneumatic base.

Installation of any high-pressure components requires that a high-pressure leak check be performed. It is best to perform the leak check prior to replacing any insulation removed during the disassembly. To perform the leak check the pressurization subsystem is charged to

operating pressure. The reactor valving is configured the same as for normal operations in the appropriate mode (single or dual line) and C8 is opened to pressurize the entire system (valve configurations are discussed in the setup procedures section). Once the reactor is pressurized to 3500 psi, S6 and C8 are closed and pressure is allowed to stabilize for 2 minutes. With pressure stabilized between 3000 and 3500 psi the gas leak rate should be less than 15 psi per minute. If the leak rate is higher the leak check procedure should be repeated individually for each section that can be isolated by valving. Once the general location of the leak is identified the exact location is determined by disassembling and plugging appropriate fitting(s), and repeating the leak check. This process continues until the leak is located and repaired.

With repairs and the leak check complete any insulation removed during disassembly must be replaced. Portions of the Fiberfrax insulation must be cut to size. The custom fit pieces are then hand molded around the section being insulated and secured with 0.02-in diameter nichrome wire.

Optical Alignment

Acquisition of spectroscopic data requires sufficient transmission of laser power through the optical cell. Optimum conditions result in transmission of 75% of the incident laser power (50% of the total laser power) through the cell. Once transmission of the incident laser power through the cell is reduced below 50%, scattering of the laser beam causes a reduction in signal intensity, and an increase in signal noise, both of which become limiting factors in analysis of the data. Under these conditions the alignment of the optical system should be verified. Figure 6 shows a schematic of the optical system used to collect spectroscopic data in the SFR.

In order to verify the alignment, fuel is pumped into the reactor with the peristaltic pumps to purge all air out of the cell. The laser is aligned through the cell by centering the beam on all delivery optics. With the beam stop on the output side of the cell removed, the beam is centered on the image of the windows transmitted through the laser-output-side of the cell. Finally, the retroreflections from the cell windows are aligned to be coincident with the incoming laser beam.

With the laser beam properly aligned through the cell, and transmission of the incident laser power through the cell between 75 and 50%, the signal image is centered on all delivery optics between the cell and the spectrometer. The pickoff lens at the signal output port of the cell should be adjusted to obtain an image of the laser beam in the cell at a distance of ~1.25-m from the centerline of the cell measured down the optical pathway with all optics installed. The imaging lens at the input to the spectrometer is set at the appropriate distance to acquire an image of the laser beam ~5-mm high by ~0.3-mm wide on the spectrometer slit.

Once the image of the laser beam in the cell is aligned to the spectrometer slit, the spectrometer must be set to the correct wavelength to continue maximizing the transmitted signal. At ambient conditions, fuel signal intensity measured at the CCD is the preferable indicator of signal transmission due to the excessive dispersion of the water Raman peak, centered at ~3628 cm^{-1}. Raman shift and the associated optimum intensities for fuels examined, as measured from the baseline at pixel 40 to the peak value, with 2W from the laser at 514.5 nm, 1-mm slit width,

and a 10-second exposure, are listed in Table 1 with typical baseline values being 1000 counts ± 500.

Alignment of the optical cell is completed using the control panel for 'CCD Control' illustrated in Figure 7. The 'Initialize' option is chosen prior to using the program for control, or if the status of the controller is questionable, to initialize the controller to known settings. Once selected this option will continue to run, as indicated by the 'Working' indicator (which indicates when the program is performing any operation), until selected again; this should be done once the 'dark' signal displayed on the CCD monitor is between 200 and 300. After initialization, in the box with the 'Scan' button, option 'Scan Mode' is set to 'Image', 'Subtraction' is set to 'Off', 'Exp. Time' is set for 10,000 (milliseconds), and the 'Scan' button is chosen. This will cause a continuously updated image to be displayed on the CCD monitor showing the spatial relationship of the signal

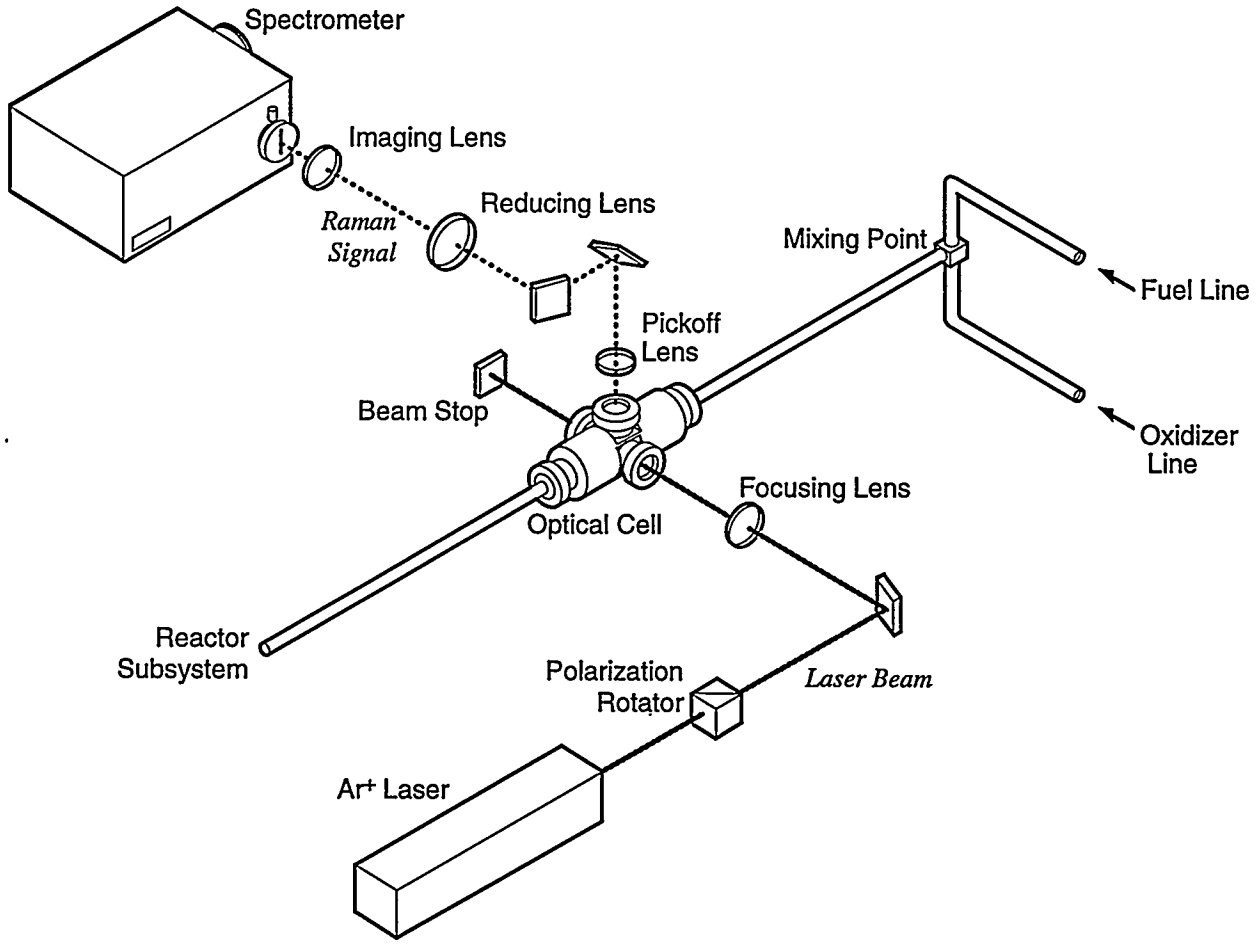


Figure 6. Schematic of the optical system used to collect spectroscopic data in the SFR.

on the CCD array. The signal is centered vertically on the CCD array using the vertical adjustment of the last turning mirror prior to the spectrometer; horizontal positioning is a function of spectrometer setting.

Table 1. Raman shift and the associated optimum intensities for Raman fuel peaks at ambient conditions with 2W at 514.5 nm from the laser, 1-mm slit width, and a 10-second exposure.

Fuel	Shift	Intensity
3 wt% Methanol	2830 cm^{-1}	2750
2 wt% Isopropanol	816 cm^{-1}	1250
2 wt% Phenol	1005 cm^{-1}	2500

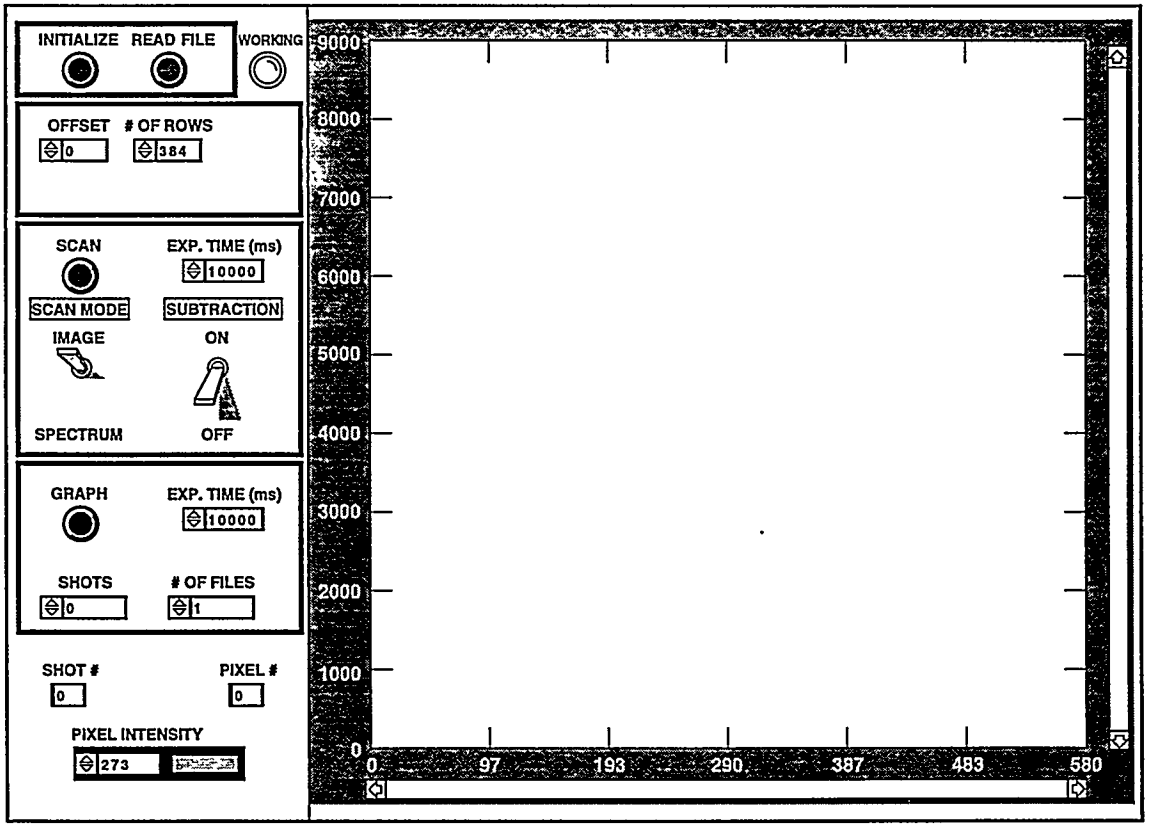


Figure 7. Control panel for the 'CCD Control' program. Control of the optical system and acquisition of optical data are accomplished using this program.

To reduce signal noise and data acquisition time the unilluminated rows of the CCD array are excluded from being read. The '# of Rows' count is reduced until the bottom of the displayed image is contiguous with the bottom edge of the signal. The 'Offset' is increased to make the top of the image contiguous with the top of the signal, and then the increase in the 'Offset' is subtracted from the reduced '# of Rows' count.

To maximize the signal, 'Scan Mode' should be set for 'Spectrum' and 'Subtraction' should be set for 'On' with the 'Scan' button still in its operational state. The laser beam image is translated across the spectrometer slit in 0.02 to 0.06 mm increments (5 to 15 divisions on the micrometer handle), between scans, using the imaging lens/translation stage adjustment at the input to the spectrometer. The translation is repeated until the signal is at maximum intensity, after which the 'Scan' button is selected to stop scanning of the CCD array.

The alignment may be documented using the controls in the box with the 'Graph' button. The 'Shots' counter refers to signal averaging and is set for the desired number of scans to be averaged. For documentation of alignment this counter is set to 1. The '# of Files' counter allows multiple, averaged, files to be acquired in one operation and is set to 1 for alignment documentation. The standard exposure time used for data acquisition is 10 s, the 'Exp. Time' counter is set to 10,000 ms to reflect this. After the counters have been set the 'Graph' button is selected and the following sequence of events is activated: a 'dark' frame is acquired, a signal frame is acquired, the dark frame is subtracted from the signal frame, the result is displayed on the CCD monitor and read into the 'CCD Control' program for display on the control panel graph, a dialog box is displayed, and the file is saved as the name entered. Throughout this sequence of events the three indicators at the bottom, left corner of the control panel display the status of the data acquisition sequence. The 'Shot #' counter displays the number of the current scan being taken, the 'Pixel #' counter displays the pixel number being read as the signal is compiled for display on the control panel graph and file acquisition, and the 'Pixel Intensity' counter displays the intensity value of the pixel whose number is indicated to the left of the intensity value. The alignment may be compared to any other compatible file by choosing the 'Read File' button. A dialog box will appear requesting a file name, once entered the requested file will be displayed on the control panel graph, replacing the previously displayed file.

Setup

Prior to conducting any experiment an experimental plan is developed. The objective of the experiment is recorded and will determine the factors to be considered. Configuration of the apparatus for the experiment, and the type and concentration of the fuel and oxidizer are determined. From these chosen concentrations, recipes are derived for feed preparation. Temperature, pressure, and flow rate parameters for the desired objective are prepared and noted. Table 2 lists single pump residence times and mass flow rates for selected pump frequencies at 3550 psi; these values are halved and doubled respectively for dual pump operations. Data analysis methods are considered, if samples will be required sample containers must be available. For optical data, Raman shifts must be researched, recorded, and converted for the spectrometer configuration in use.

Table 2. Single pump residence times and mass flow rates for selected pump frequencies at 3550 psi.

Frequency	Residence time (s)/cm^3 430 °C	470 °C	540 °C	Mass flow rate (gm/s)
12	0.70	0.57	0.46	0.17
13	0.64	0.53	0.43	0.18
15	0.56	0.46	0.37	0.21
18	0.47	0.38	0.31	0.25
21	0.40	0.33	0.27	0.30
24	0.35	0.29	0.23	0.34
30	0.28	0.23	0.19	0.42
40	0.21	0.17	0.14	0.56
55	0.15	0.13	0.10	0.77
72	0.12	0.10	0.08	1.01

Feed concentrations are prepared by weight, in 10 to 15 kg quantities, on an Ohaus I-10 scale, accurate to ± 5 gm. With the scale turned on and zeroed, a 20 liter container is placed on the scale and fitted with a funnel after which the scale is tared. The correct amount of concentrated chemical for the total weight of feed solution desired is added first; fuels are spectrophotometric grade purity and the oxidizer is mixed from 30 wt% semiconductor grade hydrogen peroxide. Water is added up to the total weight desired and the container is sealed and shaken to assure adequate mixing. Care should be taken after this step to assure that the oxidizer container is vented to prevent pressurization due to decomposition of the hydrogen peroxide. Feed compatibility with the peristaltic tubing must be confirmed with each change in feed materials and/or concentrations.

Preparation of the apparatus for the reactor start up phase of the experiment commences with energizing the electronic equipment required for the experiment. The laser, CCD-camera, and the CCD-camera controller should be turned on first, in that order, to allow time for stabilization if optical data are included in the day's experimental plan. The IBM computer used for data acquisition is turned on; the Macintosh is only started if optical data will be collected. The AO valve actuation switches, temperature controllers, and pressure monitor located in the two system control electronics racks, are powered on by the 'System Power' key located on the System Control Panel. After the control electronics are energized, the pressurization subsystem is pressurized for operation. The buffer-gas cylinder, located near the pressurization subsystem, is opened to allow flow of the buffer-gas to the compressor. At the System Control Panel valves C2, C5, and C6 are actuated, allowing gas flow to valve C8 which separates the pressurization subsystem from the reactor apparatus. Switch C3 is now actuated to provide pneumatic drive pressure to the compressor. Between one and two minutes are required for the compressor's setpoint of 8000

psi to be reached; this time is dependent on cylinder delivery pressure. Each cylinder of buffer-gas begins with a charge of ~2200 psi, and is utilized until delivery pressure is below 1000 psi (monitored as P1 on the 'SFR' control screen illustrated later as Figure 8).

Once the pressurization subsystem has reached its setpoint the inlet regulator must be set to control the pressure of the incoming buffer-gas. The normally open emergency depressurization AO valve (S5) is actuated to close the system and valve C8 is actuated to pressurize the separator. The stabilized pressure that the separator reaches is the inlet regulator setpoint. This setpoint should be ~100 psi below the pressure noted in the experimental plan. If the setpoint is too low, pressure regulator control switch R2 is used to increase the setpoint to the desired value. If the setpoint is too high, valve C8 must be closed and the separator vented by opening valve S6. Pressure regulator control switch R2 is used to decrease the setpoint, S6 is closed and C8 is reopened to pressurize the separator again. This procedure is iterated until the desired setpoint is achieved. With the regulator at the appropriate setpoint, C8 is closed and the separator is vented by opening S6 (at this point S5 may remain closed).

Preparing the feed system for experimental operations begins with filling the reservoirs with the appropriate fluids. Each reservoir position in the feed subsystem is designated with generic nomenclature for the general nature of the feed; these designations are: fuel, diluent, and oxidizer. To avoid ambiguities, and maintain compliance with Sandia's Corporate Chemical Hygiene Plan (Pigg, 1991), each reservoir must be specifically labeled precisely for the chemical and concentration contained within. During the reactor start up phase, distilled water from the reservoir designated diluent flows through the entire reactor. The three-way manual valve between each reservoir position is set to allow flow to the reactor from the diluent reservoir. The feed valve at the bottom of each reservoir is opened to allow flow to the peristaltic pumps. Both peristaltic pumps are turned on and set to run at about half speed.

Before fluid is allowed to flow through the reactor, effluent containment must be in place. A 15-gallon, poly-lined container is placed on a secondary containment pallet underneath the effluent exhaust line. Proper labeling of this container is a necessity to document the contents for later analysis and disposal. Labeling should reflect the types and highest concentration levels of fuel. Compatible chemicals may be mixed in the effluent container provided the labeling reflects the appropriate chemicals. Effluent collection containers should be replaced when the fluid level reaches ~2-in from the top.

To complete the setup phase, documentation of the experiment being conducted must be prepared. The experimental plan is entered in the log book. If optical data are to be taken, 'CCD Control' is started, and a folder designated by the date of the experiment (i.e. 1/1/95) is opened in the folder 'Current Spectra' on the Macintosh IIfx.

Reactor Start Up

Prior to pressurization it is necessary to verify that the high-pressure pumps are not cavitated. Compressed air is opened to the high-pressure pumps by actuating AO valve S10 to operate

HP1 and AO valve S11 to operate HP2. The metering valve used to meter compressed air flow to one high-pressure pump is opened to cycle that pump. Air pressure monitored on the test gauge installed next to the metering valve in use should reach 30 psi within 10 strokes, indicating pressurization of the high-pressure line. Under no circumstances should air pressure monitored on the test gauge be allowed to surpass 55 psi, as this will result in the rupture of a burst disk. Failure to achieve pressurization of the high-pressure line indicates a cavitation condition. To decavitate a high-pressure pump all air in the working volume of the pump must be eliminated by loosening the 1/4-in high-pressure fitting on the output side of the pump and cycling the pump, allowing liquid to flow through the pump, until all air has been expelled. The high-pressure fitting is then tightened and pump decavitation is verified. This procedure is repeated for each pump until pressurization of both lines has been verified.

Proper setup of the reactor valving is essential for safe and effective operation. At the System Control Panel, AO valves S1 and S2 are actuated (for single line operation, the AO valve for the preheat line in use is the only one activated). AO valve S8, between the counterflow heat exchanger and the separator, is actuated and the manual metering valve in the backpressure regulator/manual metering valve assembly must be closed.

Pressurization is accomplished by filling the reactor with water through the high-pressure pumps. With compressed air opened to the high-pressure pumps, the metering valve used to meter compressed air flow is opened to two-thirds of full scale. Within 10 minutes the reactor is filled with liquid and high-pressure operation begins. The backpressure regulator begins relieving pressure at its setpoint controlling the pressure generated by the high-pressure pumps. The backpressure regulator setpoint is adjusted, as necessary, using pressure regulator control R1 to obtain the operating pressure noted in the experimental plan $\pm$ 500 psi. Air flow to the high-pressure pumps is then adjusted to obtain an intermediate flow rate (~30 cycles per minute); this aids in the transfer of heat from the tubing to the feed fluid without excessive cooling of the reactor.

The pressurization subsystem is opened to the separator, by actuating C8, to allow buffer-gas into the system. The metering valve parallel to the backpressure regulator is adjusted to obtain a small, constant flow of buffer-gas into the separator. Operating pressure is controlled at the metering valve from this point.

With pressurized flow established, heating to operational temperatures is initiated. The control program 'SFR', controls setpoints for all fluid temperature controllers. Four options are available for controlling setpoints. Referring to Figure 8, option 'Chng SP' may be used to set each channel to its unique setpoint or all channels to one specific setpoint. The 'Zero' option can be used to zero all fluid temperature setpoints. 'Load' is used to load a preset setpoint configuration and 'Save' saves the current setpoint configuration for use with the 'Load' option. The remaining menu options are: 'Rescan'; for reinitialization of the fluid temperature controllers, 'Calib'; for pressure transducer data calibration, and 'Start'; for launching data acquisition. Option 'Start' toggles to 'Stop' and initiates a time stamp clock in the upper right hand corner while data acquisition is in progress.

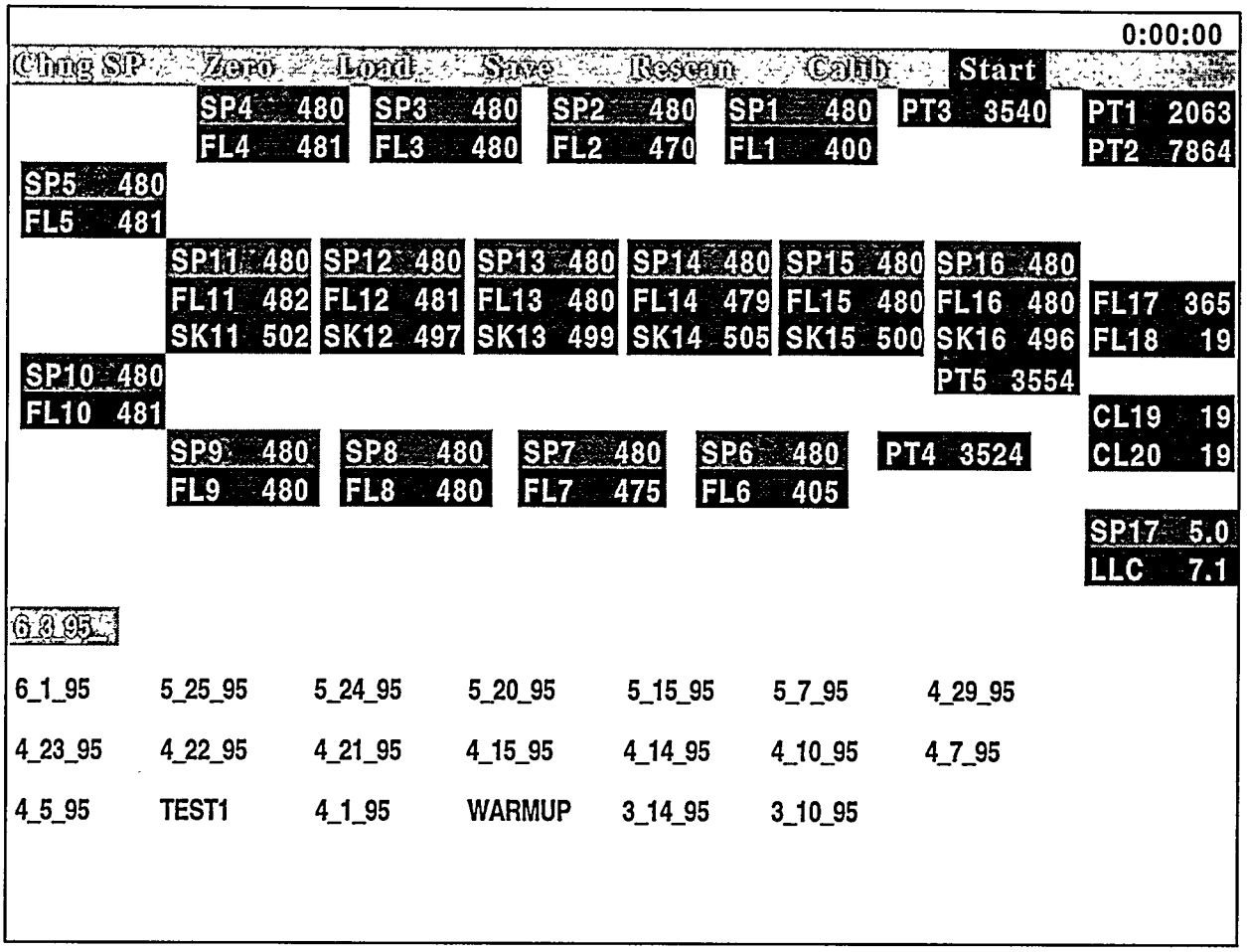


Figure 8. Computer screen for control program 'SFR'. Control of the reactor heaters and acquisition of temperature and pressure data are accomplished from this screen.

A temporal profile of the reactor heat up, acquired with the high-pressure pumps running at 30 cycles per minute, is shown in Figure 9. Temperature increase, with respect to time, is linear until the supercritical phase transition at approximately 35 minutes, between 35 and 45 minutes little heating of the fluid occurs due to the high heat capacity of the fluid. Heating of the fluid resumes after the supercritical phase transition, however, with the optical cell installed, systematic heat losses begin approaching the heating capacity of the system at approximately 450 °C resulting in a significant reduction in heat transfer to the fluid. During operations without the optical cell installed in the reactor subsystem, the limiting factor in heating the fluid is the yield strength of the high-pressure tubing at temperature. A typical thermal profile, after establishing operational conditions, is shown in Figure 10 as a function of distance from the entrance to the preheaters. The preheat subsystems extend for the first 300 cm, after which the fluid is mixed and enters the reactor subsystem which extends from 300 cm to 700 cm.

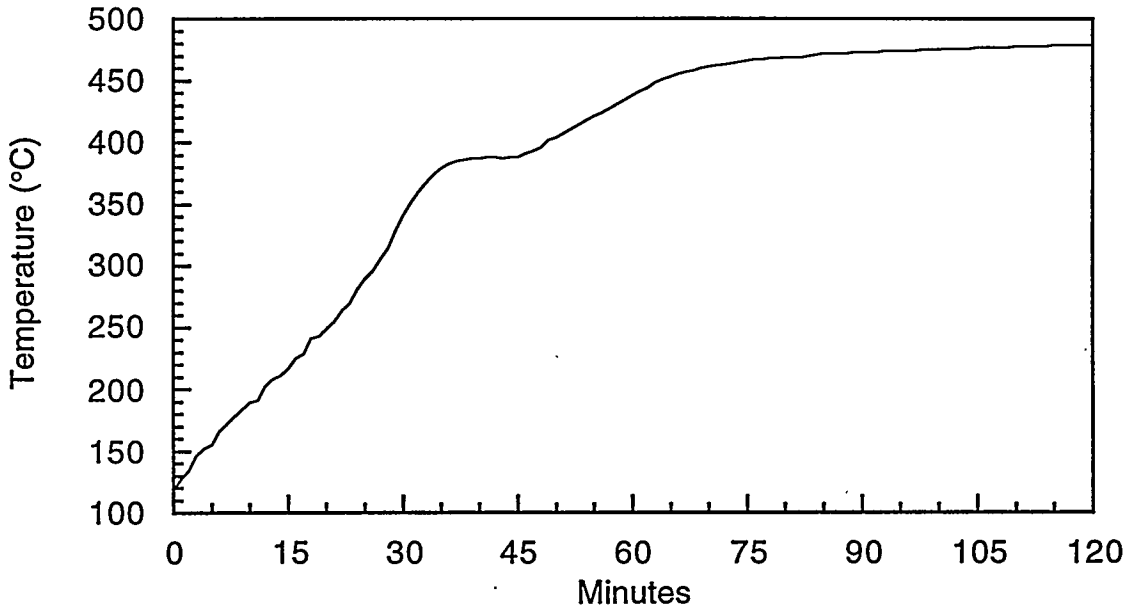


Figure 9. Heating profile of the SFR (as measured at the optical cell) with respect to time. The optical cell is the limiting factor in heating the SFR to operational conditions.

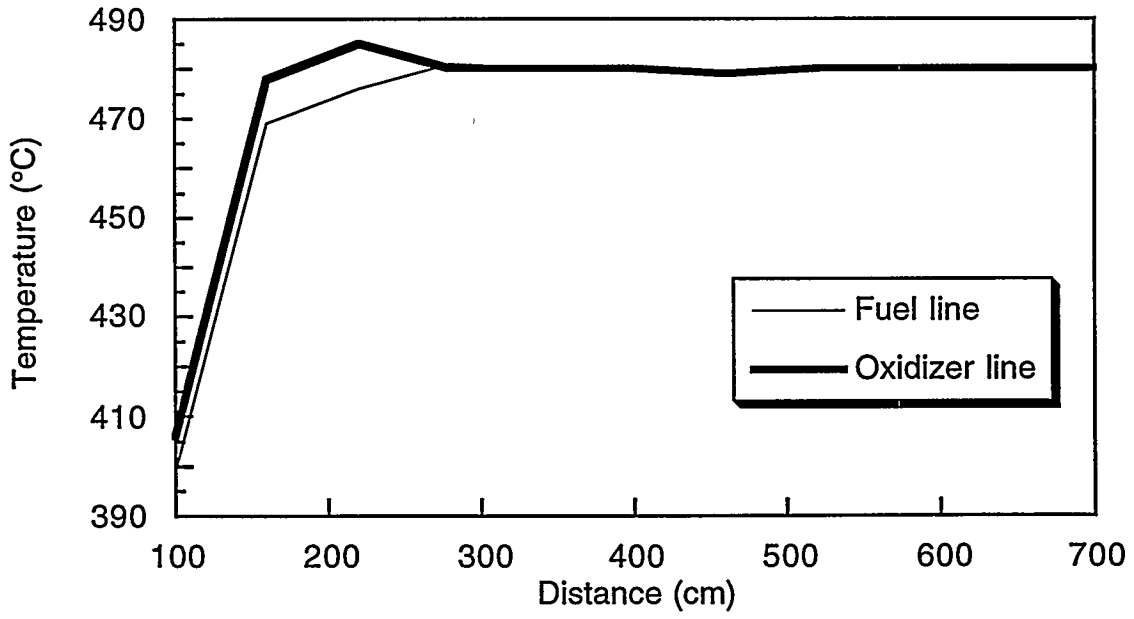


Figure 10. Temperature profiles of the parallel preheat subsystems (0-300 cm) and reactor subsystem (300-700 cm) at operational conditions.

Experimental

With isothermal supercritical conditions established in the reactor subsystem, experimental operations may begin. Temperatures must be checked, and adjusted if necessary, for instabilities. Adjustments in 1 to 2 °C increments, using control program 'SFR', are typical. Larger adjustments may be necessary as systematic heat losses approach the heating capacity of the system. Heat release during oxidation, which has been measured as high as 30 °C, must be controlled to maintain isothermal conditions. This is accomplished using a combination of fluid temperature setpoints and the manually controlled convection coolers installed on the reactor tubing.

The backpressure regulator/manual metering valve assembly is used to establish a stabilized pressure within ± 100 psi of the operational parameter set in the experimental plan. Coarse adjustments in pressure setpoint are made at the System Control Panel by adjusting the backpressure regulator setting with pressure regulator control R1. Fine adjustments are made with changes at the manual metering valve.

For faster response to fuel and oxidizer introduction into the system, flow rates are set at the highest flow rate in the experimental plan, unless otherwise specified. Emphasis should be placed first on matching piston frequencies to each other, and second, to matching the specified frequency. Piston frequency is a function of the flow rate of compressed air to the pump. Adjustments to the metering valve determine the piston frequency. During adjustment, piston frequency is averaged over ~12 seconds. For data collection purposes piston frequency is averaged over ~30 seconds.

With experimental parameters stabilized, data acquisition begins. The 'Start' option in control program 'SFR' is initiated. Temperature, pressure, and experimental time (t) data are stored in a file designated by the date of the experiment in DOS format (i.e. 1_1_95; the extension is added automatically). This file is named at the start time for data acquisition as part of the 'Start' subroutine. The start time for this file designates t = 0. The first sample and/or Raman spectrum is taken at this time.

Typically each sample taken throughout the experiment should contain ~100 ml and is labeled by date, sample number, t, temperature, and flow rate. Each spectrum taken throughout the experiment is given a file name designated by its chronological order and t (i.e. 3-0.12, where 3 is the third spectrum taken during that experiment and t is 0 hours and 12 minutes). A spectrum of the O-H stretch from water, centered at ~3628 cm^{-1}, (illustrated in Figure 11) is recorded to document repeatability of the alignment between data points. A background spectrum of the spectral region associated with the fuel Raman shift is then recorded for subtraction during data analysis. Fuel is introduced to the reactor, and after equilibration of the fuel concentration has been established, a second sample is taken and/or a fuel spectrum is recorded to calibrate 0% oxidation. Once calibrated for the fuel signal with no oxidizer present, the oxidizer is introduced into the reactor. The optical alignment is confirmed before and after each fuel spectrum by recording a 'water spectrum'.

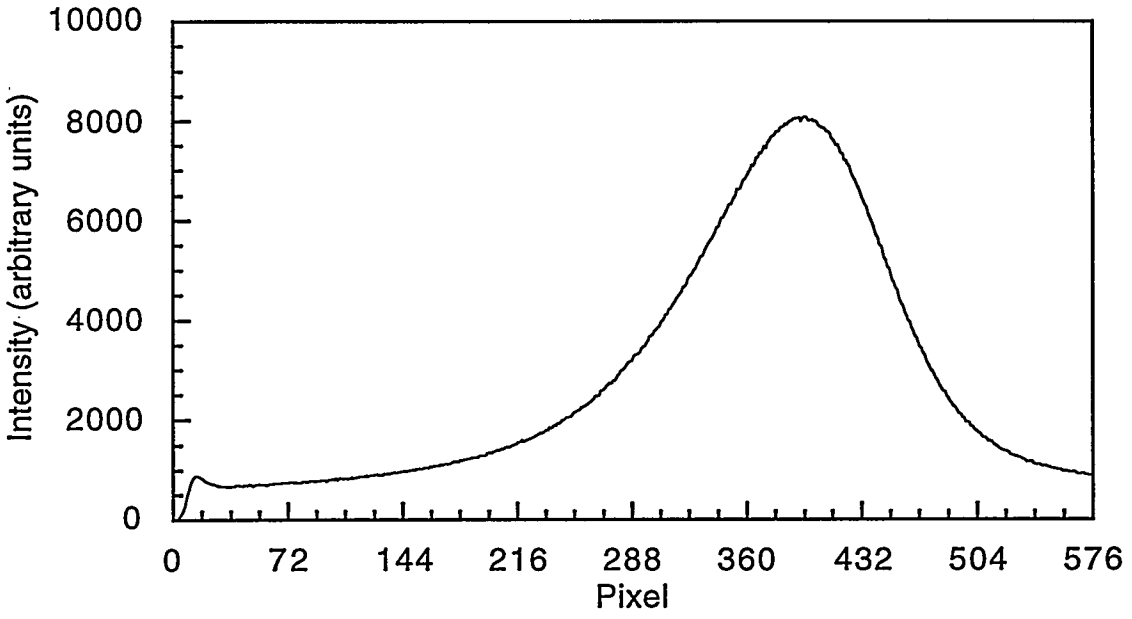


Figure 11. 3628 cm^{-1} Raman peak of water used to verify alignment at operational conditions. This spectrum was acquired at 450 °C with a 10-second exposure.

At supercritical conditions, water provides a signal superior to that of the fuel for determining alignment and transmission characteristics, due to the high percentage present and the decrease in bandwidth of the water Raman feature. A maximum water signal of 8000 counts with a 10 s exposure and 45% of the 2W of laser power through the cell is standard. Signal strengths below 75% of optimum, warrant investigation to determine the cause of degradation. Either misalignment of the optical system, loss of transmission through the windows, or a combination of both may be responsible for reduction in signal strength. To determine the cause, alignment must be checked. Failure to correct the problem after realigning the laser through the cell indicates the probability of transmission losses.

Realignment with the cell heated and pressurized must be conducted without entering the reactor enclosure due to the hazard presented by the brittle sapphire windows. The turning mirror that directs the laser into the cell is mounted on a translation stage equipped with a manually controlled remote drive on one axis. The remote drive is used to intentionally misalign the laser until the backscatter from the body of the cell is detected. From this point the mirror is translated 0.078-in in the opposite direction to center it on the window. Centering of the image on the delivery optics and spectrometer slit is verified and corrected as necessary, after which the signal maximizing procedure discussed in the maintenance section is used to attain the maximum signal available.

As samples and/or Raman spectra are collected, the corresponding temperature, pressure, and flow rate are recorded in the experimental log book as a function of t. Upon completing collection of

data for a single point, the flow rate is changed to establish a new residence time and the procedure is repeated. Once data for the obtainable range of flow rates have been recorded the entire process is repeated at new temperature conditions.

Shutdown

After completion of the experiment, data acquisition by 'SFR' is terminated, using the 'Stop' option, and the reactor is shutdown in the following order. The buffer-gas to the separator is valved off by deactivating C8 and pressure is reduced slowly through the manual metering valve installed in parallel to the backpressure regulator. While pressure is dropping, the heater setpoints are zeroed, removing power input to the heaters. As pressure continues to drop, the high-pressure pumps remain on, maintaining flow through the reactor, until the pressure reaches ~1000 psi at which point they are shut off. With the reactor at ambient pressure and flow stopped, the ancillary equipment (i.e. peristaltic pumps, pressurization subsystem, control electronics, etc.) is de-energized, the 'System Power' key switch is shutoff, and control programs 'SFR' and 'CCD Control' are exited.

Certain conditions such as leaks, control failures, and cavitation of the high-pressure pumps may also warrant an unforeseen shutdown of the apparatus. Under these circumstances the same shutdown procedure is used. In the case of extreme emergencies such as earthquake or fire, an emergency power shutoff is provided next to each exit.

ANALYSIS

The SFR has been used to examine the processing characteristics of a variety of materials over a range of operational parameters. Subjects of interest include chemical kinetics and model development, feasibility evaluations, inorganic salt deposition phenomena, and reactor materials corrosion. To examine this variety of different aspects of supercritical water oxidation, a number of analytical methods have been used. Table 3 lists materials examined in the SFR and the analysis methods used for each material.

Several of the feasibility experiments conducted using the SFR were designed to evaluate destruction efficiency based simply on total organic carbon (TOC) remaining in the liquid effluent. TOC is defined as all carbon in the solution that does not exist as CO or CO_2. In practice, TOC is detected as all carbon that cannot be removed by acidification and sparging. In these experiments, approximately 100 ml samples are collected. The analytical equipment requires 3 - 10 ml aliquots for each point and good lab practice dictates checking and double checking each sample. Two different analytical instruments have been used, an Astro 2001 and a Rosemount 3290. Both instruments work on the principle of acidification of the solution to drive out dissolved CO_2 followed by oxidation. A calibrated infrared detector is then used to measure the quantity of CO_2 created by the oxidation.

Table 3. Materials examined in the SFR and analysis methods used.

	TOC	GC	Ion probe	pH probe	Turbidity	Raman
Acetic acid	x					
Blue dye	x				x	
Ethylene glycol	x					
Green dye	x				x	
Isopropanol		x				x
Latex paint	x				x	
Methanol	x	x				x
Methylene chloride	x					
Methyl ethyl ketone	x					
Motor oil	x				x	
Orange dye	x		x	x	x	
Phenol	x					x
Potassium chloride			x			
Red dye	x		x	x	x	
Roundup® herbicide	x					
Smoke green pyro	x		x	x	x	
Sodium chloride			x		x	
Sodium hydroxide			x	x	x	
Sodium phosphate			x			
Sodium sulfate			x	x		
1,1,1 Trichloroethane	x					

Other projects have called for monitoring the oxidation of the specific organic fuel compound. Gas chromatography (GC) is used to monitor the presence of a specific species quantitatively. GC analysis is conducted using a Poraplot Q column (0.53 mm bore x 10 m) in an HP 5890 gas chromatograph. Quantitative measurements were obtained using a flame ionization detector (FID) with helium as the carrier gas. In general, gas chromatography of low molecular weight organics is difficult with water as the solvent. Same sample reproducibility was about ± 10%. Minimum sample detectability was approximately 100 ppm for methanol, as an example.

A variety of chemical analysis tools are used to analyze the inorganic composition of the liquid effluent. These include ion specific electrodes, pH meters, and 'wet chemistry' kits accompanied by turbidity (spectrophotometric) measurement.

The ion specific electrodes have been used to detect sodium, potassium, chlorine, and sulfate ions in the 1-2000 ppm range. These electrodes are used to measure an electrochemical voltage which can be calibrated to a concentration of a specific ion. In these experiments, liquid effluent samples are collected for a short period of time, primarily from the sample line. The concentration of salt is then correlated to changes in the reactor conditions upstream. These methods have been used to monitor salt deposition rates for NaCl, KCl, and Na_2SO_4 (LaJeunesse, et al., 1993a; LaJeunesse, et al., 1993b) and develop an empirical description of salt deposition in tubular reactors (Chan, et al., 1994).

The analytical kits are used to monitor transition element concentrations and have been useful in developing qualitative models for corrosion in the reactor. Specifically, these kits have been used to detect parts-per-billion range of chromium, nickel, and molybdenum. The methods involve obtaining a sample, adjusting pH, and mixing specific reagents to generate intensely colored solutions. The coloration is quantified by using a small narrow band filter spectrometer and correlated to an original ion concentration by way of a calibration table. These methods have allowed for a detailed model of how corrosion depends on fuel and oxidizer concentration in the processing of dyes (LaJeunesse, et al., 1995).

Much of the work in the SFR is focused on collecting data for the development of chemical kinetic mechanisms that can describe the detailed characteristics of the oxidation of simple organic species in supercritical water. These data need to include not only the measurement of the loss of the initial fuel species, but also the production and subsequent consumption of key intermediates. This is achieved by using an in situ diagnostic based on Raman spectroscopy.

To generate the Raman scattering signal, the probe volume is pumped with an argon ion laser. The beam is focused into a cell, described above, with a 500-mm focal length lens producing a pump beam diameter of approximately 0.06 mm. The scattered light is collected with f/3 aperture and imaged through a lens and mirror system onto the input slit of the spectrometer. To aid in rejection of the scattered laser light, an additional colored glass filter (RG 570) is employed in front of the spectrometer. The relevant portion of the Raman spectrum is imaged onto the CCD array. The resulting Raman signal is collected, processed, and stored using the 'CCD Control' program.

The power of the Raman signal, P_r, can be expressed as

$$P_r = P_i n\left(\frac{\partial\sigma}{\partial\Omega}\right)\Omega\ell\varepsilon \tag{1}$$

where P_i is the pump laser power, n is the species number density, $\frac{\partial\sigma}{\partial\Omega}$ is the differential Raman cross section, Ω is the collection solid angle, ℓ is the sampling extent, and ε is the collection efficiency. It is evident that the Raman signal power is directly proportional to the species number density. Therefore, by integrating the observed Raman transition, a value which is proportional to the species concentration can be obtained. In addition, it has been shown that the Raman signal intensity is independent of the surrounding species concentrations at these water densities, meaning that the absolute concentration of a species can be calculated following calibration of the system.

The optical system is calibrated by flowing a known concentration of the compound to be examined, without oxidizer, through the optical module and recording the resulting Raman signal. To account for any drifts in the system alignment which could affect the absolute magnitude of the signal over time, all species signals are ratioed to the O-H stretch from water, centered at ~3628 cm^{-1}, which was collected immediately prior to the species signal. Water can be used as an internal standard since it is in great excess for all experiments and as a result, its concentration will remain approximately constant during a constant temperature experimental run. Therefore, by normalizing the species signal by the water signal any drift in the system parameters noted above are properly accounted for, with the exception of the temperature dependence of the differential cross section.

One important technical consideration, even for a non-reacting sample, is that the calibration of the experiment is slightly temperature dependent. The absolute concentrations of water and fuel change with absolute density, but their relative concentrations do not and therefore, the ratio of their concentrations should remain constant as should the ratio of their integrated Raman signals. However, because there may be different temperature dependencies of the differential Raman cross sections for fuel and water, a calibration at a single temperature , which establishes a ratio of water to fuel signal for an unreacted sample, is not valid at all temperatures. To account for this variation on temperature dependence, nearly 20% from 440 °C to 500 °C, Raman signals for the experimental compound and water are collected at temperatures from 440 to 500 °C. Using the ratio of these signals a calibration curve can be constructed that accounts for the temperature affect; all subsequent measurements are then corrected accordingly. Since pressure is constant within 2 % for all runs and the integrated Raman signal is linearly dependent on density, the small fluctuations in pressure will not significantly affect the results.

Concentrations are calculated by integrating the area under the Raman peak and applying the appropriate calibration. When two slightly overlapping peaks are present, as is the case with methanol and formaldehyde, an approximation must be made to perform the integration. In this case the area of each peak is calculated by integrating from the tail of the peak to the minimum point of their overlapping region. Since the amount of overlap between the methanol and formaldehyde peaks is small, the error in this approximation is insignificant relative to the noise on the data. In a related investigation, with a higher degree of peak overlap, the error in the area

determination, for a worst case scenario, was estimated to be less than 10%. The uncertainty in determining the concentration from the integration of a single peak, based solely on a statistical analysis of the noise associated with the measurement technique, is less than ± 2.5% of full scale. As an example, this sets the minimum detection limit at about 1/20 of the unreacted concentration of 1.5 wt % methanol or 2.3 $x10^{-3}$ moles/liter at typical experimental conditions.

PERFORMANCE

In order to insure accuracy of the data generated by the SFR, tests are run to characterize performance attributes of the reactor. Pressure, temperature, residence times, chemistry effects, and sampling techniques have been examined to assure that data are not affected by the apparatus or measurement techniques.

Typically, pressure is constant throughout the system and one calibrated pressure transducer is sufficient for generating accurate pressure data. However, conditions can exist in the SFR which can create pressure differentials throughout the reactor. Installed valves prevent uniform pressurization when closed, and plugs created by deposition of inorganic fuel components in the reactor can constrict flow enough to generate large pressure differentials. To assure uniform pressurization, transducers are installed to measure and record pressure in each section which may be isolated by a valve. Once flow is established and verified, pressure differentials as shown in Figure 12, are used to detect plugging in the reactor, aiding in the performance of experiments on salt deposition in tubular reactors (LaJeunesse, et al., 1993a; LaJeunesse, et al., 1993b).

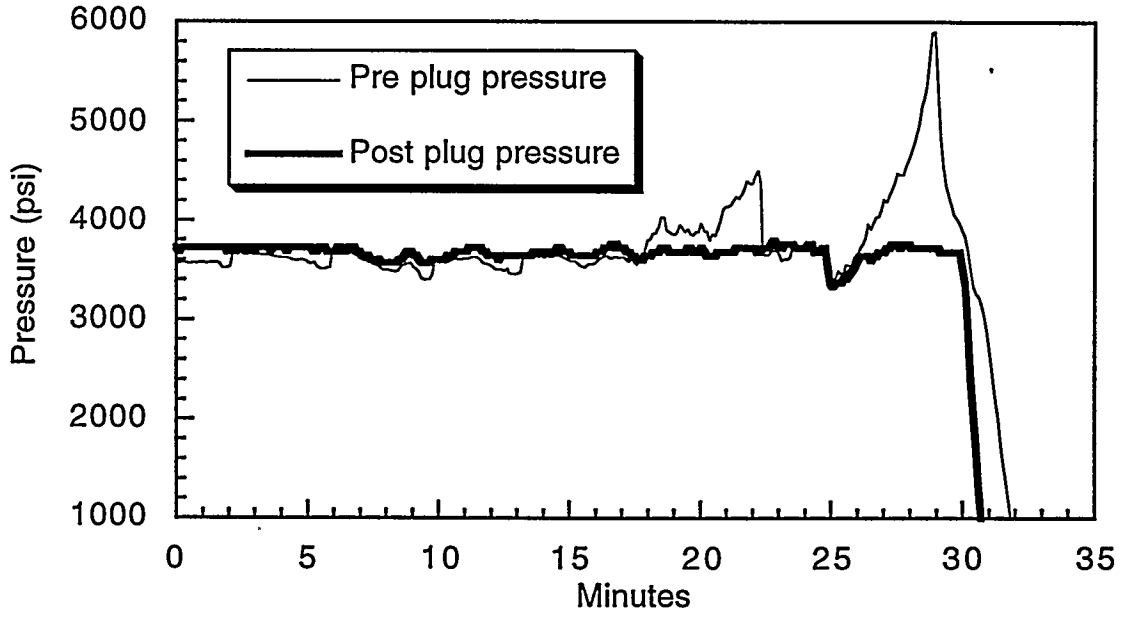


Figure 12. Pressure differential generated by plugging, as a result of inorganic solids deposition in the reactor.

Temperatures are measured approximately every half meter throughout the heated sections of the reactor. Variations from the controller setpoints, typically ± 2 °C, are recorded and, when greater than the 0.075% Type K thermocouple limit of error, are compensated for during data analysis. Thermal profiles of the reacting fluids are monitored and adjusted to maintain isothermal conditions as high as 580 °C. Installation of the optical cell decreases the range over which isothermal conditions can be maintained. Due to excessive heat losses at the cell, isothermal conditions above 540 °C are inaccessible.

Due to the degradation of thermocouple junctions in the reactor environment, Inconel 600 sheathed thermocouples are used to protect the junction. To measure the effect of heat conduction down the thermocouple sheathing from the fitting, a thermocouple with the sheathing stripped away from the junction was inserted into the flow less than 1 mm from one of the standard thermocouples. Differentials measured were within the Type K thermocouples limit of error.

Residence times, t_{res}, are calculated as a function of reacting distance, fluid density at reaction conditions calculated from an equation of state, the cross sectional area of the reactor, and mass flow rate by

$$t_{res} = \frac{L_r \rho_{rxn} A_r}{\dot{m}} \tag{2}$$

where L_r = reacting distance, ρ_{rxn} = fluid density at reaction conditions, A_r = cross sectional area of the reactor and $\dot{m}$ = mass flow rate. Mass flow rates are calculated, using a plug flow approximation, as a function of pump volume, fluid density, and piston frequency by

$$\dot{m} = V_p n \rho_{amb} \nu \tag{3}$$

where V_p = pump volume, n = number of pumps (1 or 2), ρ_{amb} = fluid density at ambient conditions, and ν = pump frequency in Hz. Pump volumes were calibrated by measuring the fluid output over 500 cycles and averaging. This experiment was repeated three times with repeatability within 1%. Pump rates are limited to a minimum of 10 cycles per minute by the air flow needed to maintain consistent pump frequency, and a maximum of 80 cycles per minute by the capacity of the system to transfer heat to the fluid. The distance measured for residence time calculation is dependent on the data acquisition method being used to determine species concentrations. Effluent sample residence times are calculated using the full 3.8 meter length of the reactor. When Raman spectroscopy is being employed, residence time is dependent on the distance from the mixing point to the incident laser.

Corrosion effects on the reactor itself must also be monitored. Levels of chromium and nickel, both components of the Inconel 625 tubing, as high as 6.8 ppm and 51 ppm respectively have been measured with certain feeds. Reactor tubing sections were pressure tested to 100,000 psi after 2 years of use and showed no signs of degradation.

As fuels are heated they may be subject to a chemical change brought about by heat affecting the composition of the fuel stream and reacting stream through pyrolysis or hydrolysis

reactions. These reactions are capable of reducing the fuel concentration by means other than SCWO. In order to measure pyrolysis, an experimental run is conducted on each new fuel being examined. Fuel concentrations are measured at low supercritical temperatures. As temperature is increased through the entire range being examined, concentrations are measured and compared to the low temperature reference. A decrease in concentration is an indication of pyrolysis. If pyrolysis is found to be a concern, the fuel may be heated by injecting a higher concentration of fuel into the preheated water stream immediately prior to mixing.

The role of the reactor walls in the oxidation process needs to be considered. Holgate and Tester (1994a) addressed this problem for H_2 and CO oxidation. They determined, despite a relatively small reactor diameter (0.16 cm), that the walls do not significantly affect the results because of the very high fluid densities employed. That is, the relative number of wall collisions a reactant experiences is small compared to the number of collisions it experiences with another reactant. These conclusions were supported by experimental results using a packed reactor.

The SFR has an internal diameter that is three times greater than that used by Holgate and Tester (1994a). In addition, because of the lower experimental temperatures employed in the SFR, the fluid densities are greater. From experimental conditions collision rates may be calculated for walls and other reactant molecules from kinetic theory. The frequency of molecular collisions per unit volume in an ideal gas is given by

$$Z_A = \frac{\sigma \bar{u} \rho^2}{\sqrt{2}} \tag{4}$$

and the frequency of wall collisions per unit area is given by

$$Z_W = \frac{\bar{u} \rho}{4} \tag{5}$$

where Z is the collision frequency, $\bar{u}$ is the mean molecular velocity, ρ is the molecular density, and σ is the molecular cross section (Moore, 1972). Taking the ratio of Z_W/Z_A and multiplying by the surface area to volume ratio of the reactor (which for a tube is 4/d, where d is the diameter) gives the fraction of collisions a molecule experiences, η, with a wall relative to those experienced with other species,

$$\eta = \frac{\sqrt{2}}{\rho \sigma d}. \tag{6}$$

Evaluating Equation 6 for typical current experimental conditions, $\rho = 5$ mol/L or 3×10^{21} cm^{-3}, d = 0.48 cm, and $\sigma = 6.5 \times 10^{-16}$ cm^2 for water, yields $\eta = 1.5 \times 10^{-6}$. This indicates that a molecule has over 10^5 collisions within the fluid per wall collision. To compare this to other ambient–pressure, high–temperature flow reactors, note that the ratio is inversely proportional to d and ρ. For typical experimental conditions employed in a past atmospheric pressure analysis of CO and H_2 oxidation, i.e., d = 10.32 cm and temperature $\approx$ 1000 K (Yetter, et al., 1991),

using $\sigma = 7.7 \times 10^{-16}$ cm^2 (for N_2) and $\rho = 0.012$ mol/L or 7.3×10^{18} cm^{-3} (for an ideal gas) gives $\eta = 2.4 \times 10^{-5}$. This corresponds to an equivalent reactor diameter for our conditions of 0.03 cm. Since this is over an order of magnitude smaller than the reactor diameter, it is safe to conclude that wall reactions have minimal impact on experimental results.

Analysis of effluent samples in the SFR necessitates the calculation of the throughput time, which is defined as the time for the sample to flow from the high-pressure pump to the acquisition port. To calculate these times the reactor is divided into zones. Each zone is either at ambient or operational conditions. The residence time in a zone is calculated using a plug flow approximation and the appropriate density, as in Equations 2 and 3 (which are defined for operational conditions). The change in temperature, from ambient to operational conditions, between zones occurred over a relatively small distance and was therefore neglected. Table 4 shows the calculated sample line throughput times for selected dual pump frequencies.

Table 4. Calculated sample line throughput times for selected dual pump frequencies.

Frequency	Throughput time (min) 430 °C	470 °C	540 °C
12	4.9	4.7	4.6
13	4.5	4.4	4.2
15	3.9	3.8	3.7
18	3.3	3.2	3.1
21	2.8	2.7	2.6
24	2.4	2.4	2.3
30	2.0	1.9	1.8
40	1.5	1.4	1.4
55	1.1	1.0	1.0
72	0.8	0.8	0.8

Samples may be taken from either of two lines, the main effluent line or a sample line which bypasses the separator to eliminate the possibility of mixing with stagnant effluent. Concentrations were measured from both lines to determine the effect of sampling from the main effluent line. Concentrations from the main effluent line were diluted by as much as 20% from the concentrations taken at the sample line demonstrating that samples from the main effluent line are only reliable for time averaged concentration measurements.

Two types of flow conditions occur when taking samples from the sample line. At low flow rates the effluent drips into the sample container, however, at higher flows the liquid effluent is atomized by the gaseous effluent exiting the line. Volatile organics being examined may be subject to evaporation under these conditions. A comparison of these conditions was undertaken by establishing steady conditions in the reactor and taking samples from both states in random order. Figure 13 shows that a 10% variation in the samples did not correspond to changes in these conditions, and furthermore that repeatability in the analysis of the samples was less sensitive than the sampling method.

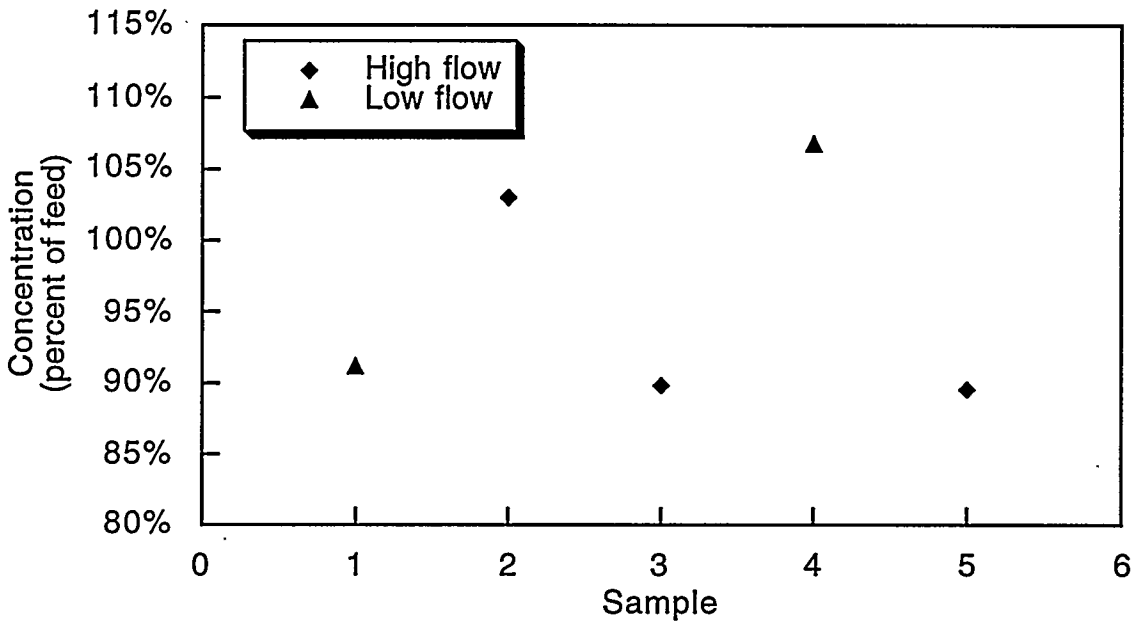


Figure 13. Comparison of fuel concentrations measured at varying sample line flow rates.

SUMMARY

The SFR is used to conduct chemical oxidation experiments at temperatures and pressures above the critical point of water. It consists of 7 operational subsystems. Flow begins in the feed subsystem and is pressurized and heated in the preheat subsystems. Reactions occur in the reactor subsystem and are then cooled to ambient temperature in the cool down subsystem prior to separation of the solids, gases, and liquids in the separation subsystem. The pressurization subsystem provides pressurized inert buffer-gas to dilute excess oxygen and aid in pressure control. An optical cell is installed in the reactor subsystem for collection of Raman spectroscopy data.

Reactor control and data acquisition are accomplished through a combination of valves, electronics, computers, and software. Valves are used to isolate sections of the reactor whenever necessary. Thermocouples monitor temperatures, and transducers are used for monitoring pressure throughout the reactor. These data are transmitted to a multiplexer for computer control and data acquisition by a custom written C+ program. A custom written LabView program controls and records Raman spectroscopy acquisition.

Procedures for conducting experiments in the SFR are divided into six categories: maintenance, optical alignment, setup, reactor start up, experimental, and shutdown. Maintenance activities are those performed between experiments to maintain the reactor in operating condition. Optical alignment procedures must be completed when acquisition of spectroscopic data is desired. Setup operations involve definition and preparation of a specific experiment. Reactor start up procedures establish operational pressure and temperature conditions in the reactor. Experimental activities are carried out for collection of experimental data. Shutdown procedures are followed at the end of an experiment to de-energize the equipment.

The SFR has been used to examine the processing characteristics of a variety of materials over a range of operational parameters. Subjects of interest include chemical kinetics and model development, feasibility evaluations, inorganic salt deposition phenomena, and reactor materials corrosion. To examine this variety of different aspects of supercritical water oxidation, a number of analytical methods have been used. Total organic carbon analysis has been used to measure organic carbon remaining in the effluent after processing to determine destruction efficiencies of organic compounds. Gas chromatography is used to monitor the presence of a specific species quantitatively. A variety of chemical analysis tools are used to analyze the inorganic composition of the liquid effluent. These include ion specific electrodes, pH meters, and 'wet chemistry' kits accompanied by turbidity measurement. Much of the work in the SFR is focused on collecting data for the development of chemical kinetic mechanisms that can describe the detailed characteristics of the oxidation of simple organic species in supercritical water. These data need to include not only the measurement of the loss of the initial fuel species, but also the production and subsequent consumption of key intermediates. This is achieved by using an in situ diagnostic based on Raman spectroscopy.

In order to insure accuracy of the data generated by the SFR, tests are run to characterize performance attributes of the reactor. Pressure, temperature, residence times, chemistry effects, and sampling techniques have been examined to assure that data are not affected by the apparatus or measurement techniques.

Transducers are installed to measure and record pressure in each section which may be isolated by a valve to assure uniform pressurization. Temperatures are measured approximately every half meter throughout the heated sections of the reactor and tests have been conducted to verify the accuracy of fluid temperature measurements.

Residence times are calculated as a function of reacting distance, fluid density at reaction conditions, the cross sectional area of the reactor, and mass flow rate; mass flow rates are calculated, using a plug flow approximation, as a function of pump volume, fluid density, and piston frequency. Pump volumes were calibrated by measuring the fluid output over

500 cycles and averaging.

Corrosion effects on the reactor itself have been monitored and reactor tubing sections were pressure tested to 100,000 psi after 2 years of use and showed no signs of degradation. Pyrolysis reactions are capable of reducing the fuel concentration by means other than SCWO. If pyrolysis is found to be a concern the fuel may be heated by injecting a higher concentration of fuel into the preheated water stream immediately prior to mixing. The role of the reactor walls in the oxidation process needs to be considered. It has been determined that the walls do not significantly affect the results because of the very high fluid densities employed. That is, the relative number of wall collisions a reactant experiences is small compared to the number of collisions it experiences with another reactant. These conclusions have been supported by experimental results using a packed reactor (Holgate and Tester, 1994a).

Throughput times of the feeds, from pump to sample acquisition, have been calculated to assure that samples taken are subject to the conditions intended. Concentrations were measured from both the sample and main effluent lines to determine the effect of sampling from the main effluent line. Concentrations from the main effluent line were diluted by as much as 20% from the concentrations taken at the sample line. Volatile organics being examined may be subject to evaporation under high flow conditions upon exiting the sample line. A comparison of high and low flow conditions was undertaken and a 10% variation in the samples did not correspond to changes in these conditions.

The SFR is a highly adaptable tool for examining engineering, process, and fundamental chemistry issues regarding the development of SCWO. Extreme care has been taken to insure the consistency and the accuracy of the data generated with this apparatus. By applying the operational procedures outlined in this document, and considering the performance characteristics discussed, a high degree of confidence may be placed in the data generated and the conclusions drawn from it.

REFERENCES

Chan, J.P.; LaJeunesse, C.A.; Rice, S.F. Experimental Techniques to Determine Salt Formation and Deposition in Supercritical Water Oxidation Reactors. Fire, Combustion, and Hazardous Waste Processing. Acharya, S.; Annamalai, K.; Presser, C.; Skocypec, R. D., Eds.; ASME, 296:171-176; 1994.

LaJeunesse, C. A.; Rice, S. F.; Hanush, R. G.; Aiken, J. D. Salt Deposition Studies in a Supercritical Water Oxidation Reactor (Interim Report). Sandia National Laboratories, Livermore, CA; 1993.

LaJeunesse, C. A.; Chan, J. P.; Raber, T. N.; Macmillan, D. C.; Rice, S. F.; Tschritter, K. L. Supercritical Water Oxidation of Colored Smoke, Dye, and Pyrotechnic Compositions. Final Report: Pilot Plant Conceptual Design. Sandia National Laboratories, Livermore, CA; 1993.

LaJeunesse, C.A.; Mills, B.E.; Rice, S.F. Case Study on the Destruction of Organic Dyes in Supercritical Water. Presented at "Chemical Oxidation: Technology for the Nineties", Nashville TN, February 15-17, 1995, (to be published as monograph).

Moore, W. J. Physical Chemistry. Prentice-Hall: Englewood Cliffs, NJ; 1972.

Pigg, C. J. Corporate Chemical Hygiene Plan (PN471001A). Sandia National Laboratories, Livermore, CA; 1991.

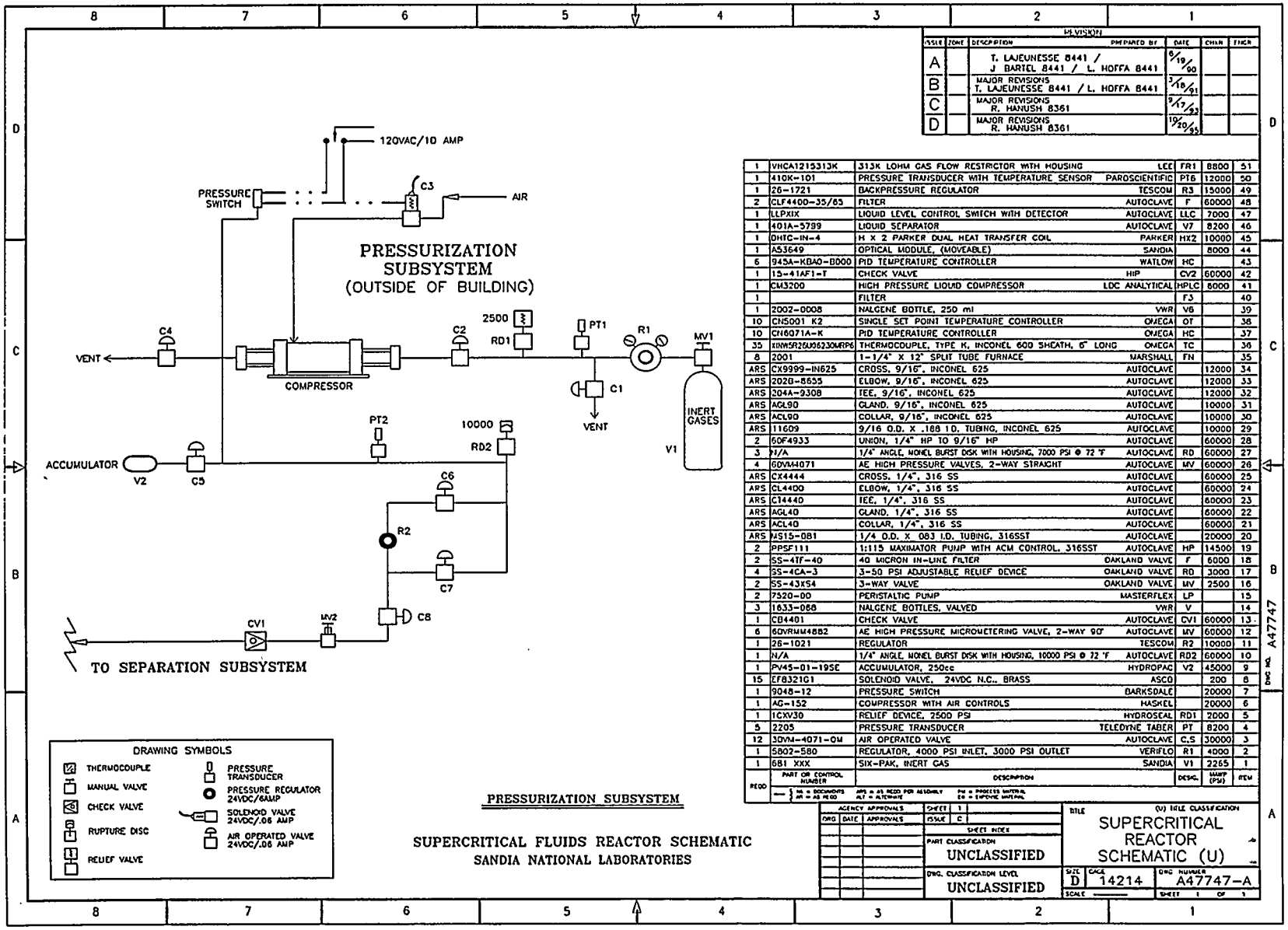
Sandia Pressure Safety Manual (MN47100E). Sandia National Laboratories, Livermore, Ca.; 1995.

Tester, J. W.; Holgate, H. R.; Armellini, F. J.; Webley, P. A.; Killilea, W. R.; Hong, G. T.; Barner, H. E. Chapter 3, Supercritical Water Oxidation Technology Process Development and Fundamental Research. In: Emerging Technologies in Hazardous Waste Management III ; Tedder, D. W. and Pohland, F. G., Eds.; American Chemical Society: Washington DC, 518:35-76;1991.

Yetter, R. A.; Dreyer, F. L.; Rabitz, H. Flow Reactor Studies of Carbon Monoxide/Hydrogen/Oxygen Kinetics. Combust. Sci. Technol. 79:129-140;1991.

APPENDIX

A



PRESSURIZATION SUBSYSTEM

SUPERCRITICAL FLUIDS REACTOR SCHEMATIC
SANDIA NATIONAL LABORATORIES

REVISION					
ISSUE	ZONE	DESCRIPTION / PREPARED BY	DATE	CHKD	ENGR
A		T. LAJEUNESSE 8441 / J BARTEL 8441 / L. HOFFA 8441	5/19/90		
B		MAJOR REVISIONS T. LAJEUNESSE 8441 / L. HOFFA 8441	3/18/91		
C		MAJOR REVISIONS R. HANUSH 8361	9/17/93		
D		MAJOR REVISIONS R. HANUSH 8361	10/20/95		

ITEM	PART OR CONTROL NUMBER	DESCRIPTION	DESIG.	RATING (PSI)	ITEM
1	VHCA1215313K	313K LOHM GAS FLOW RESTRICTOR WITH HOUSING LEE	FR1	8800	51
1	410K-101	PRESSURE TRANSDUCER WITH TEMPERATURE SENSOR PAROSCIENTIFIC	PT6	12000	50
1	26-1721	BACKPRESSURE REGULATOR TESCOM	R3	15000	49
2	CLF4400-35/65	FILTER AUTOCLAVE	F	60000	48
1	LLPXIX	LIQUID LEVEL CONTROL SWITCH WITH DETECTOR AUTOCLAVE	LLC	7000	47
1	401A-5799	LIQUID SEPARATOR AUTOCLAVE	V7	8200	46
1	DHTC-IN-4	H X 2 PARKER DUAL HEAT TRANSFER COIL PARKER	HX2	10000	45
1	A53649	OPTICAL MODULE, (MOVEABLE) SANDIA		8000	44
6	945A-KBA0-B000	PID TEMPERATURE CONTROLLER WATLOW	HC		43
1	15-41AF1-T	CHECK VALVE HIP	CV2	60000	42
1	CM3200	HIGH PRESSURE LIQUID COMPRESSOR LDC ANALYTICAL	HPLC	8000	41
1		FILTER	F3		40
1	2002-0008	NALGENE BOTTLE, 250 ml VWR	V6		39
10	CN5001 K2	SINGLE SET POINT TEMPERATURE CONTROLLER OMEGA	OT		38
10	CN6071A-K	PID TEMPERATURE CONTROLLER OMEGA	HC		37
35	XRM5R26U06230URP6	THERMOCOUPLE, TYPE K, INCONEL 600 SHEATH, 6" LONG OMEGA	TC		36
8	2001	1-1/4" X 12" SPLIT TUBE FURNACE MARSHALL	FN		35
ARS	CX9999-IN625	CROSS, 9/16", INCONEL 625 AUTOCLAVE		12000	34
ARS	202B-8655	ELBOW, 9/16", INCONEL 625 AUTOCLAVE		12000	33
ARS	204A-9308	IEE, 9/16", INCONEL 625 AUTOCLAVE		12000	32
ARS	AGL90	GLAND, 9/16", INCONEL 625 AUTOCLAVE		10000	31
ARS	ACL90	COLLAR, 9/16", INCONEL 625 AUTOCLAVE		10000	30
ARS	11609	9/16 O.D. X .188 I.D. TUBING, INCONEL 625 AUTOCLAVE		10000	29
2	60F4933	UNION, 1/4" HP TO 9/16" HP AUTOCLAVE		60000	28
3	N/A	1/4" ANGLE, MONEL BURST DISK WITH HOUSING, 7000 PSI @ 72 °F AUTOCLAVE	RD	60000	27
4	60VM4071	AE HIGH PRESSURE VALVES, 2-WAY STRAIGHT AUTOCLAVE	MV	60000	26
ARS	CX4444	CROSS, 1/4", 316 SS AUTOCLAVE		60000	25
ARS	CL4400	ELBOW, 1/4", 316 SS AUTOCLAVE		60000	24
ARS	CI4440	IEE, 1/4", 316 SS AUTOCLAVE		60000	23
ARS	AGL40	GLAND, 1/4", 316 SS AUTOCLAVE		60000	22
ARS	ACL40	COLLAR, 1/4", 316 SS AUTOCLAVE		60000	21
ARS	MS15-081	1/4 O.D. X .083 I.D. TUBING, 316SST AUTOCLAVE		20000	20
2	PPSF111	1:115 MAXIMATOR PUMP WITH ACM CONTROL, 316SST AUTOCLAVE	HP	14500	19
2	SS-4TF-40	40 MICRON IN-LINE FILTER OAKLAND VALVE	F	6000	18
4	SS-4CA-3	3-50 PSI ADJUSTABLE RELIEF DEVICE OAKLAND VALVE	RD	3000	17
2	SS-43XS4	3-WAY VALVE OAKLAND VALVE	MV	2500	16
2	7520-00	PERISTALTIC PUMP MASTERFLEX	LP		15
3	1633-068	NALGENE BOTTLES, VALVED VWR	V		14
1	CB4401	CHECK VALVE AUTOCLAVE	CV1	60000	13
6	60VRMM4882	AE HIGH PRESSURE MICROMETERING VALVE, 2-WAY 90° AUTOCLAVE	MV	60000	12
1	26-1021	REGULATOR TESCOM	R2	10000	11
1	N/A	1/4" ANGLE, MONEL BURST DISK WITH HOUSING, 10000 PSI @ 72 °F AUTOCLAVE	RD2	60000	10
1	PV45-01-195E	ACCUMULATOR, 250cc HYDROPAC	V2	45000	9
15	EF8321G1	SOLENOID VALVE, 24VDC N.C., BRASS ASCO		200	8
1	9048-12	PRESSURE SWITCH BARKSDALE		20000	7
1	AG-152	COMPRESSOR WITH AIR CONTROLS HASKEL		20000	6
1	1CXV30	RELIEF DEVICE, 2500 PSI HYDROSEAL	RD1	2000	5
5	2205	PRESSURE TRANSDUCER TELEDYNE TABER	PT	8200	4
12	30VM-4071-0M	AIR OPERATED VALVE AUTOCLAVE	C,S	30000	3
1	5802-580	REGULATOR, 4000 PSI INLET, 3000 PSI OUTLET VERIFLO	R1	4000	2
1	681 XXX	SIX-PAK, INERT GAS SANDIA	V1	2265	1

REQD: — = NA = DOCUMENTS AR = AS REQD; APS = AS REQD PER ASSEMBLY ALT = ALTERNATE; PM = PROCESS MATERIAL EQ = EXPOSE MATERIAL

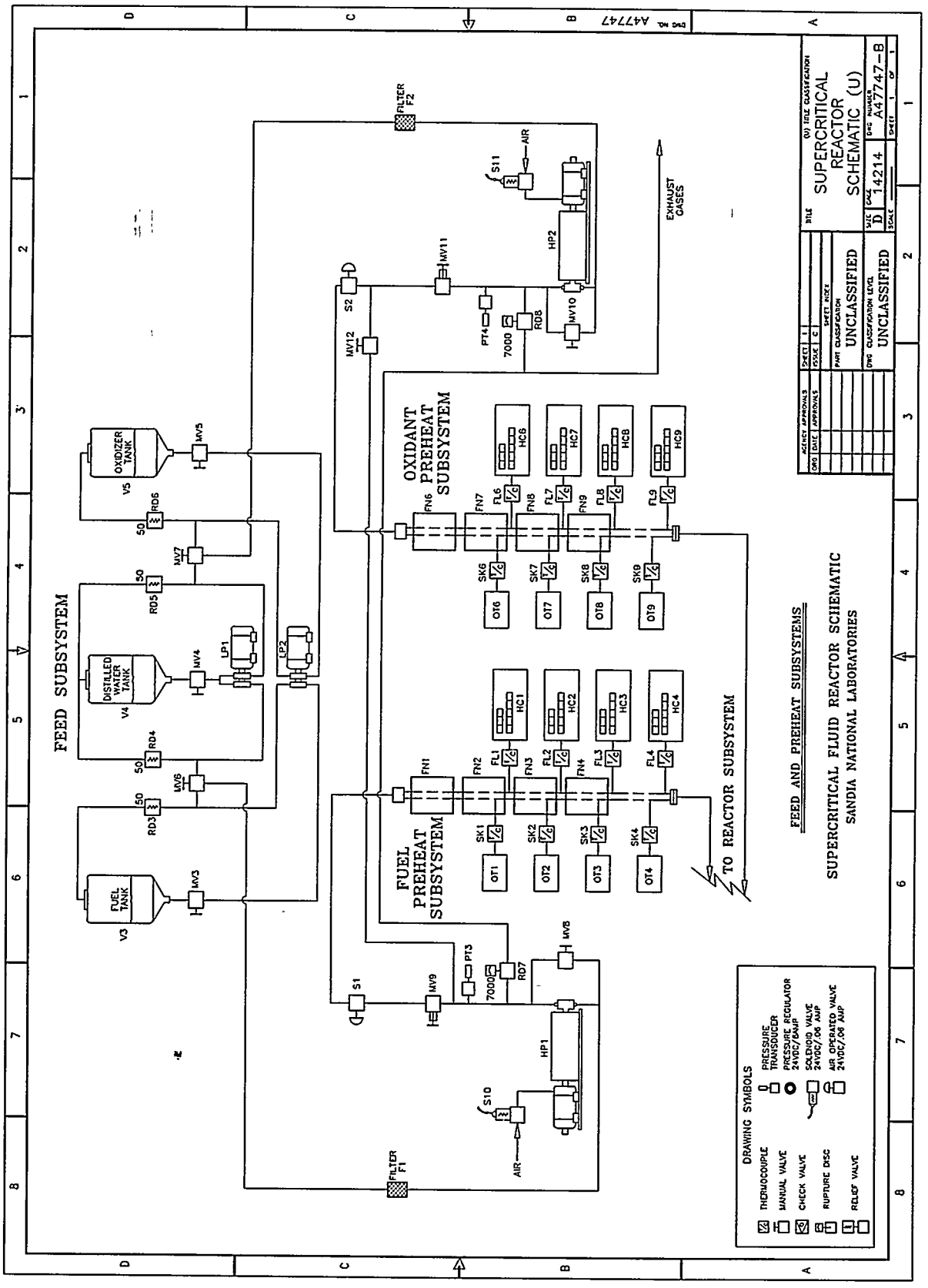
AGENCY APPROVALS		
ORG	DATE	APPROVALS

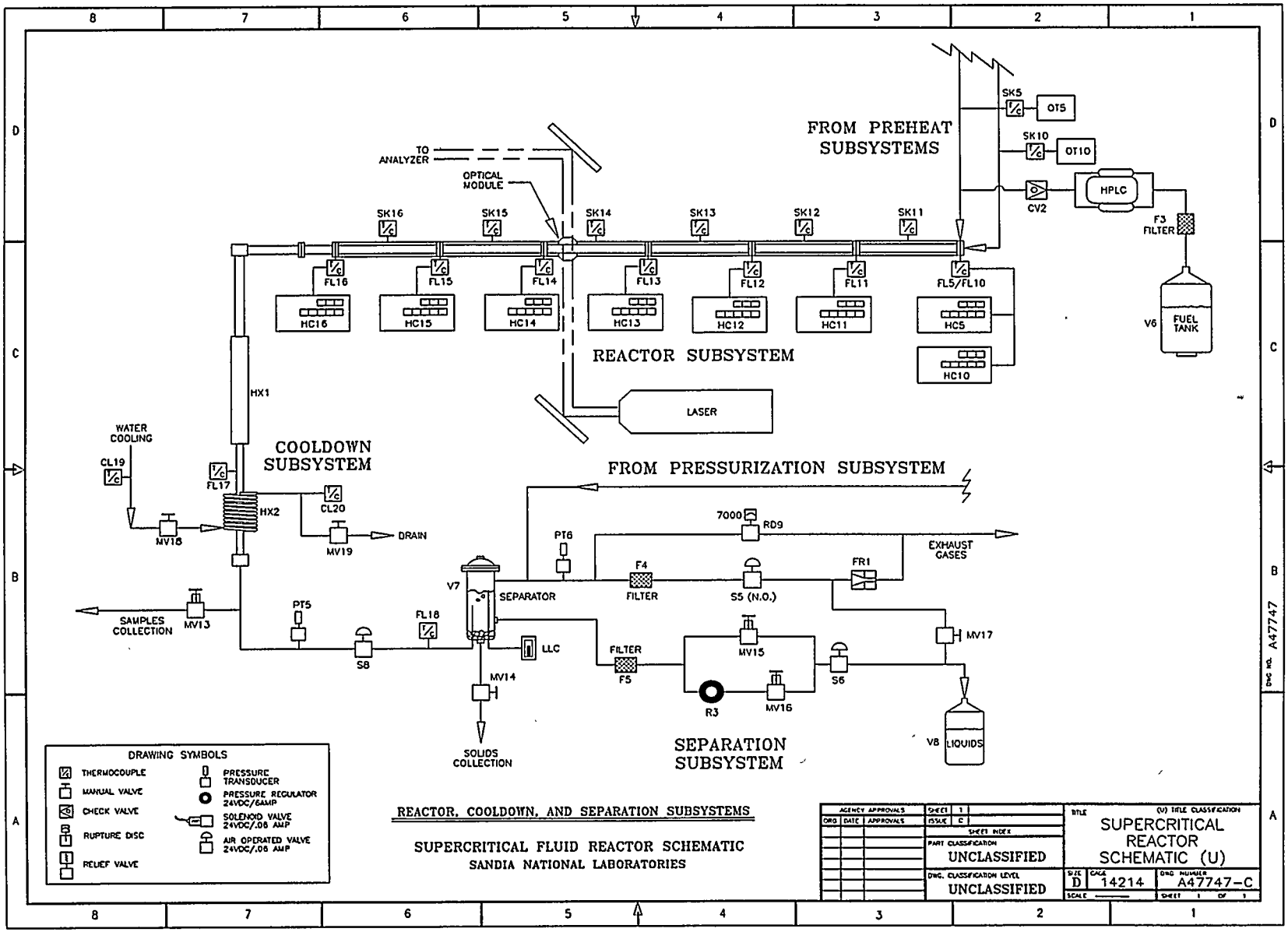
SHEET 1
ISSUE C
SHEET INDEX
PART CLASSIFICATION: UNCLASSIFIED
DWG. CLASSIFICATION LEVEL: UNCLASSIFIED

TITLE: (U) TITLE CLASSIFICATION
SUPERCRITICAL REACTOR SCHEMATIC (U)

SIZE D | CAGE 14214 | DWG NUMBER A47747-A
SCALE —— | SHEET 1 OF 1

DWG NO. A47747


FEED SUBSYSTEM
OXIDANT PREHEAT SUBSYSTEM
FUEL PREHEAT SUBSYSTEM
TO REACTOR SUBSYSTEM
FEED AND PREHEAT SUBSYSTEMS
SUPERCRITICAL FLUID REACTOR SCHEMATIC
SANDIA NATIONAL LABORATORIES
SUPERCRITICAL REACTOR SCHEMATIC (U)
UNCLASSIFIED
A477747-B
EXHAUST GASES
AIR
DRAWING SYMBOLS
THERMOCOUPLE
MANUAL VALVE
CHECK VALVE
RUPTURE DISC
RELIEF VALVE
PRESSURE TRANSDUCER
PRESSURE REGULATOR 24VDC/6AMP
SOLENOID VALVE 24VDC/.06 AMP
AIR OPERATED VALVE 24VDC/.06 AMP


FROM PREHEAT SUBSYSTEMS
TO ANALYZER
OPTICAL MODULE
SK5
OT5
SK10
OT10
HPLC
CV2
F3 FILTER
SK16
SK15
SK14
SK13
SK12
SK11
FL16
FL15
FL14
FL13
FL12
FL11
FL5/FL10
HC16
HC15
HC14
HC13
HC12
HC11
HC5
HC10
V6 FUEL TANK
REACTOR SUBSYSTEM
LASER
HX1
WATER COOLING
CL19
FL17
COOLDOWN SUBSYSTEM
HX2
CL20
MV18
MV19
DRAIN
FROM PRESSURIZATION SUBSYSTEM
7000
RD9
EXHAUST GASES
PT6
F4
FILTER
S5 (N.O.)
FR1
V7
SEPARATOR
SAMPLES COLLECTION
MV13
PT5
FL18
S8
LLC
FILTER
F5
MV15
MV17
S6
MV14
R3
MV16
V8 LIQUIDS
SOLIDS COLLECTION
SEPARATION SUBSYSTEM
DRAWING SYMBOLS
THERMOCOUPLE
MANUAL VALVE
CHECK VALVE
RUPTURE DISC
RELIEF VALVE
PRESSURE TRANSDUCER
PRESSURE REGULATOR 24VDC/6AMP
SOLENOID VALVE 24VDC/.06 AMP
AIR OPERATED VALVE 24VDC/.06 AMP
REACTOR, COOLDOWN, AND SEPARATION SUBSYSTEMS
SUPERCRITICAL FLUID REACTOR SCHEMATIC
SANDIA NATIONAL LABORATORIES
AGENCY APPROVALS
ORG DATE APPROVALS
SHEET 1
ISSUE C
SHEET INDEX
PART CLASSIFICATION
UNCLASSIFIED
DWG. CLASSIFICATION LEVEL
UNCLASSIFIED
(U) TITLE CLASSIFICATION
TITLE
SUPERCRITICAL REACTOR SCHEMATIC (U)
SIZE D
CAGE 14214
DWG NUMBER A47747-C
SCALE
SHEET 1 OF 1
DWG NO. A47747

UNLIMITED DISTRIBUTION

Jim Hurley
US AF AL/EQS
139 Barnes Drive, Suite 8000
Tyndall Air Force Base, FL 32403

Dr. Robert Shaw
Chemical & Biological Sciences Div.
U.S. Army Research Office
Research Triangle Park, NC 27709-2211

Joan F. Brennecke
University of Notre Dame
Department of Chemical Engineering
Notre Dame, IN 46556

Dr. Kenneth Brezinsky
Dept. Of Mechanical and Aerospace Engineering
Princeton University
PO Box CN5263
Princeton, NJ 08544-5263

Prof. Klaus Ebert
Kernforschungszentrum Karisruhe
Institut fur Heisse Chemie
Postfach 3640
D-76021 Karlsruhe
Germany

Dr. Earnest F. Gloyna
University of Texas at Austin
Environmental and Health Engineering
Austin, TX 78712

Dr. Phillip E. Savage
University of Michigan
Chemical Engineering Department
Herbert H. Dow Building
Ann Arbor, MI 48109-2136

Carl Adema
SERDP Program Office
Program Manager for Compliance and Global Environmental Change
901 North Stuart Street, Suite 303
Arlington, VA 22203

Trienel Aheam
Labat-Anderson Incorporated
8000 Westpark Dr.
Suite 400
McLeain, VA 22102

K.S. Ahluwalia
Foster Wheeler Development Corporation
Engineering Science & Technology
12 Peach Tree Hill Road
Livingston, NJ 07039

Dr. Steven J. Buelow
CST-6
Los Alamos National Lab.
Los Alamos, NM 87545

Dr. David A. Hazelbeck
General Atomics
M/S 15-100D
3550 General Atomics Court
San Diego, CA 92121-1194

Dr. Glenn T. Hong
MODAR, Inc.
14 Tech Circle
Natick, MA 01760

W. Killilea
MODAR, Inc.
14 Tech Circle
Natick, MA 01760

Richard Kirts
Naval Civil Engineering Laboratory
560 Laboratory Dr.
Port Hueneme, CA 93043-4328

Richard C. Lyon
Eco Waste Technologies
2305 Donley Drive
Suite 108
Austin, TX 78758-4535

Dr. Michael Modell
Modell Environmental Corporation
300 5th Avenue, 4th Floor
Waltham, MA 02154

Dr. Jean Robert Richard
CNRS
Combustion Laboratory
1C Avenue de la Recherche Scient.
Orleans 45071
France

Crane Robinson
Arament Research
Development & Engineering Center
(ARDEC)
SMCAR-AES-P
Building 321
Picatinny Arsenal, NJ 07806-5000

Dr. Gregory J. Rosasco
Nat'l Institute of Standards and
Technology
Division 836, Bldg. 221, Rm B-312
Gaithersburgh, MD 20899

Prof. Jefferson W. Tester
Massachusetts Institute of Technology
Energy Laboratory
Room E40-455
77 Massachusetts Avenue
Cambridge, MA 02139

Phil Whiting
Abitibi-Price Inc.
2240 Speakman Drive
Mississauga, Ontario L5K 1A9
Canada

Marvin F. Young
Aerojet
PO Box 13222
Sacramento, CA 95813-6000

MS9001	T. O. Hunter,8000
Attn:	D. L. Crawford, 1900
	E. E. Ives, 5200
	M. E. John, 8100
	L. A. West, 8600
	R. C. Wayne, 8700
MS9054	W. J. McLean, 8300
MS9051	L. A. Rahn, 8351
MS9055	F. P. Tully, 8353
MS9056	G. A. Fisk, 8355
MS9052	D.R. Hardesty, 8361
Attn:	S. W. Allendorf
	M. D. Allendorf
	L. L. Baxter
MS9052	J. D. Aiken, 8361
MS9052	R. G. Hanush, 8361
MS9052	T. B. Hunter, 8361
MS9052	S. F. Rice, 8361
MS9053	R. R. Steeper, 8362
MS9053	R. W. Carling, 8362
MS9053	R. J. Gallagher, 8366
MS9105	L. A. Hiles, 8400
MS9406	B. Haroldsen, 8412
MS9406	H. H. Hirano, 8412
MS9406	C. LaJeunesse, 8412
MS9406	M. C. Stoddard, 8412
MS9404	B. E. Mills, 8713
MS9021	Technical Communications Department, 8535, for OSTI (10)
MS9021	Technical Communications Department, 8535/Technical Library, MS0899, 13414
MS0899	Technical Library, 13414 (4)
MS9018	Central Technical Files, 8523-2 (3)

Org.	Bldg.	Name	Rec'd by	Org.	Bldg.	Name	Rec'd by

LS 2900-QE

Sandia National Laboratories