

Gas Phase Ester Reduction System

Standard Operating Procedure

Lab: Davenport 270

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Section 1: Overview

Type of SOP: Process Hazardous Material Hazardous Class of Materials Equipment

Synopsis:

The purpose of this SOP is to provide guidelines and safety procedures for the Gas Phase Ester Reduction System.

Section 2: Risk Assessment Summary (Hazards and control measures)

Information obtained from performing a risk assessment should be entered into this section.

Materials:

Material (name, CAS #, other ID)	Hazards
Hydrogen	Flammable, asphyxiant
Ethyl acetate	Flammable
Propyl acetate	Flammable
Nitrogen	Asphixiant especially at high pressures
Helium	Asphixiant especially at high pressures

Relevant References for Material Hazards:

Hydrogen
<http://airgas.com/msds/001026.pdf>

Helium
<https://www.airgas.com/msds/001025.pdf>

Nitrogen
<https://www.airgas.com/msds/001040.pdf>

Ethyl Acetate
<https://fscimage.fishersci.com/msds/08750.htm>

Propyl Acetate

<https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=537438&brand=SIGALD&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsigald%2F537438%3Flang%3Den>

Equipment Hazards:

Agilent HP 6890 Gas Chromatograph—Hot surfaces, pressurized gases, electric shock

ATS Furnace—Heating elements, electric shock

Gas lines—High pressure system, hot surfaces

Teledyne Isco Syringe pump—high pressure system filled with volatile, flammable liquids, electric shock

Variacs and heating tape—Ignition source, electric shock

Hazardous Conditions:

The ventilation of vapors or gases coming out from the system is on the lab ventilation. After retightening any connection in the system, make sure to leak test the system.

The ATS Furnace can be heated up to 400 °C

H₂ dependence experiments typically include the highest total system pressure. Be aware during these conditions and inform others.

Technique Hazards:

Personal Protective Equipment

Safety glasses must be worn when operating equipment for explosion and splash hazards.

When refilling syringe pump and handling ethyl acetate (or propyl acetate), gloves must be worn. Nitrile has break through time of 42 min.

Thermal gloves should be worn when removing reactor and adjusting heating tape.

Engineering Controls

Exit gases from system are piped up into the laboratory vent system to reduce probability of inhalation.

Ethyl acetate (and propyl acetate) should be stored in flammable cabinet.

Pressure relief valves should be set on all gas lines. Hydrogen and nitrogen high pressure gas lines should be set for 980 psig. GC gas lines should be set for 100 psig. He and H₂ line near office door should be set for ~1000 psig.

Variacs and furnace should be plugged into outlets with a ground fault circuit interrupter (GFCI).

Section 3: Procedures

Startup Procedure

1. Tighten reactor with catalyst loaded.
2. Leak check the system at 980 psi for at least 2 hours. Use Snoop to check the ¼" connections. Pressure decay test must be under 0.034 psi/min. (See loading reactor procedure for more details)
3. Wrap top and bottom of reactor with heating tape and insulation.
4. Check for continuity of heating tape plugs with multimeter
5. Plug power cords in corresponding power strips.
6. Ensure all power cords are plugged in and power stripes turned on. This will start the variacs to heat the lines. Let them warm up while you're starting the rest of the system.
7. Turn on furnace main power switch (right hand side). Make sure all output switches are off (3 switches under each zone controller). Red output indicator lights should NOT be on or flashing.
8. Make sure GC gas lines are pressurized to ~80psig. Open GC gas valves on panel below computer keyboard (Air, He, H₂). Turn on GC using main power switch (bottom left hand side)—It'll go through a startup sequence checking itself. Let it run its course before doing anything else.
9. Turn on both computers. Start ChemStation Online on GC computer (only after GC is done running its startup sequence, else there will be a communication error). Open Condition Controller LabVIEW program on Controller computer (in Documents folder). Check communication ports for furnace, DAQ board, MFCs on the blue sticky note.
10. Close needle valve on nitrogen line near electronic pressure regulator. Make sure 3 way valve on N₂ line near south door is pointing up. Open main valve on N₂ tank. Delivery pressure depends on maximum pressure used on Ester reduction (gas and liquid systems) and Direct Synthesis reactor as this line is shared. Open N₂ valve on top of the system structure.
11. Close H₂ valve downstream of the tank (labeled as high pressure H₂). Open main valve on H₂ tank (third tank from right to left near office door). Set delivery pressure to < 1000 psig. Close main valve, purge line using manual pull valve. This will be loud as it exhausted into overhead exhaust lines—*warn lab mates*. Open main valve again.
12. Turn on output switches to furnace and set desired temperature. It will start ramping as soon as you set it at 5 C/min.
13. System is now ready for normal operation. Use LabVIEW program to control flow rates and pressure. Program pump with the Labview code for constant pressure or flow mode. Gradient mode is only programmable from pump front panel. Control temperature directly or through EZ Zone program.

Reloading Reactor Procedure

1. Stop GC sequence using Abort>Abort.
2. Turn 1/16" 3 way valve near liquid inlet to the left letting the pump depressurize. Liquid will squirt into small beaker. Stop program on pump.
3. Depressurize system—Set all flows to 0 on Labview. Depressurize the system using the Labview code in no less than 200 psi decrements. Higher decrements may damage the BPR diaphragm. Cycle bypass 3-way valves so there is not pressure in either the reactor or bypass.
4. Turn He flow to ~20 sccm on MFC keep flowing through bypass while you remove the reactor.
5. Turn off output switches on furnace.

6. Unplug heating tape on top and bottom reactor. Check to make sure you have the right heating tapes and aren't cooling other parts of the system. Changing temperatures back and forth with cause leaks in the compression fittings, which will make your life miserable.
7. Unwrap insulation on top and bottom of reactor. Wear insulating gloves to avoid electric shock. These should be the wide insulation pieces. On the top you also need to unwrap part of the insulation on the horizontal line up until the 1/4"- 1/8" union. Unwrap the heating tape in these areas as well. *Careful* not to twist or bend these too much as you may damage or expose the wires which could lead to shorting or applying a voltage to the system itself.
8. Open furnace (do not touch any internal part, it will be hot)
9. Unplug thermocouple from top of reactor
10. Use the compressed air line on top of the reactor to blow air over it and cool down the reactor much faster. Track the temperature with the thermocouple (it will take around 30 minutes for the reactor to cool down from 230 °C).
11. Unplug thermocouple from top of reactor.
12. Detach the reactor from the system at the 1/4"-1/8" unions (on the 1/4" side) at the edge of where you just removed the heat tape and insulation. This is specified in case those fittings need to be replaced, we always have spare parts on hand. Keep the reactor up right as you carry it to the vise—you don't want to dump the catalyst into the top portion. On the vise, use a 15/16" wrench to undo the VCR fittings on the top and bottom of the reactor. [Hold the female VCR nut in the vise, use the wrench on the male nut.] Be careful as the outside metal and pieces of glass inside may still be hot!
13. Inspect the VCR gasket. These can be saved for 5 or 6 reuses. Remove the glass tube around the thermocouple and glass rod from the bottom of the reactor—set aside to clean later.
14. Make a work station with 2 large Kimwipe to keep area and materials clean. One will be clean side for loading, the other will be trash side for unloading.
15. On a piece of weigh paper, dump out spent catalyst. Only collect catalyst, not glass wool and store in labeled vial as SPENT, catalyst name, unloading date and sequence number. Record on lab notebook.
16. Use 1/4" SS ram rod to push out remaining glass wool and catalyst. Push from top, out the bottom of the reactor. Discard the glass wool in the solid waste container.
17. Clean reactor with DI water followed by acetone (to dry faster). Make sure all debris are removed from reactor by looking straight through it. Dry with clean air. Make sure it is completely dry. You might need to dry VCR nuts with Kimwipe. Clean glass rod and tube, and reactor bottom (male VCR to 1/4" compression fitting) in similar fashion. For top set of fittings with thermocouple, use a Kimwipe with acetone and wipe down thermocouple and male VCR face. Clean the ram rod with acetone.
18. Place fritted VCR gasket in between the bottom VCR connections and finger tighten fittings together. (top is marked with a T).
19. Slide glass rod into bottom of reactor.
20. Ball up glass wool ~1/4" diameter and shove into top of reactor. Use ram-rod to force ball into reactor. Repeat until line on ram rod is *just* above top of reactor. Tap ram-rod to make sure glass wool bed firm and padded down. Recheck line. This is to ensure that the thermocouple sits in the center of the catalyst bed, and that the bed has a firm support in the center of the furnace.
21. Add 2500 mg catalyst material. If desired catalyst mass is < 2500 mg, add dry silicon carbide to the desired mass of catalyst until the total mass is 2500 mg. Carefully mix the catalyst and the silica in a weigh boat prior to adding to reactor.
22. Slide glass tube over thermocouple and slide non-fritted VCR gasket over TC assembly. Insert into top of reactor. Finger tighten top VCR fittings. Tighten VCR fittings on vise in similar fashion of disassembly. Keep reactor upright when carrying it, and slightly tilted in vise to not let the catalyst slide up the reactor. You will not over tighten it—use your whole body weight to avoid any leaks at these fittings.

23. Clean ¼” connections in the reactor side with acetone, both the inside and the threads
24. Attach back to reactor at ¼” -1/8” unions. Connect the thermocouple to the display
25. Leak test first! Pressurize the system. There are 2 ways of doing this – a fast and a slow method. **Fast method:** Send the gas through the reactor turning upstream bypass valve to the reactor side but turn downstream bypass valve pointing down. Set He MFC to 0. Flow He to the reactor by using the MFC bypass, directing bypass valves away from MFC and opening ball valve. Pressure will increase rapidly to ~1000 psig. Close ball valve and point MFC bypass valves to the MFC side. **Slow method:** Send the gas through the reactor turning upstream bypass valve to the reactor side and downstream bypass valve pointing up. Set flow in He MFC to 100% and start pressurizing the reactor from the Labview code by 200 psi increments until 980 psi. Once the pressure reaches 980 psi, point downstream bypass valve down, set He MFC flow to 0 and start the pressure decay test
26. Leak test. There are 2 ways of doing this (I recommend using both) **Pressure decay test:** Use the record function on the pressure gauge to monitor the leak rate. Leak test for at least 2 hours. Leak rate should be < 0.034 psi/min. Check ¼” compression fittings at which you removed the reactor with Snoop. Careful to not get Snoop on the insulated lines or any other electrical equipment. If you cannot tighten these fittings anymore to stop leaks, you may need to replace those pieces of ¼” tubing. Use new fittings/ferrules! Not recycled stuff in the reused box—you never know how bad a job you or your labmates may have done when they swagelocked those fittings initially. **Checking flow rate with bubble flow meter:** Set reactor pressure to 950 psig and He flow to 100 %. Measure the flow rate at the end of the reactor with the bubble flow meter. Compare the measured flow rate with the most recent calibration. If the difference between the calibration and the measured flow rate is greater than 5 sccm, inspect for leaks
27. Rewrap the heating tape and insulation on top and bottom of reactor
28. After leak checking, set the system up to do an in situ pretreatment. [Currently I use 100 sccm H₂ at 1 atm] Release the pressure in the reactor by pointing the downstream bypass valve up and decreasing pressure by 200 psi steps using the Labview code
29. After releasing the pressure, set the desired flow rates in Labview code.
30. Turn furnace main power off and back on. Open EZ-Zone configurator on Controller computer. Choose ‘Configure a device while communicating with it’. Select the COM port for the furnace. You’ll do one zone at a time. Set up a profile for pretreatment conditions. [‘Time’ is the ramp function, choose length of time to reach setpoint. ‘Soak’...soaks at given setpoint for a given time. Choose ‘End’ as the last step. This will return to the closed loop setpoint. Set the closed loop setpoint under ‘Setup’ > ‘Control Loop’ for your initial reactor temperature.] Start profile ‘Operator’>‘Profile Status’> type in profile # which you just set up>‘Profile’ on dropdown menu. Hit ‘Back’ and repeat for the other 2 zones. *Turn output switches on!*
31. If needed, refill pump. Use ester that has been dried with molecular sieve. The max syringe volume is 100 mL so estimate accordingly. Cap the bottle and move to system. Install the filter in the 1/8” line to prevent particulates to going into the pump. Wash the pump twice with about 30 ml of ester (fill 30 ml and then empty through the prime line. Refill and use downstream 1/16” 3-way valve pointing towards you to prime the line. Set a constant flow mode and wait until the flow is steady, once all the air has been evacuated, close the valve to the vertical position and stop the pump.
32. Once your pretreatment is finished, you are ready for science!

Setting up experiments

1. Use the ‘Calculations for system flowrates’ Excel Sheet to easily calculate conditions. Input the partial pressure of reactants and H₂ flow to calculate pump flow rate.
2. System is currently set to flow H₂ and He concurrently. If needed, a CO/H₂ mixture or NH₃ tank can be connected by short alterations just upstream of the top MFC within the hood.

3. If using NH_3 , make sure you have a Kalrez seal MFC for top MFC (0-10 or 0-100sccm). Double check all other components in system to make sure they are compatible with NH_3 (check valves, filters, MFCs, valves). Follow the same procedure for adding the CO/H_2 MFC EXCEPT that the delivery pressure should be 80 psig and you purge the line using the valves in the gas cabinet regulator system.
4. Setup LabVIEW program specifying total pressure and MFC flow rates for each data point interval. Input the time for each interval. Start the LabVIEW program and stop after ~30s allowing pressure and gas flowrates to stabilize while you setup the syringe pump.
5. Set the Teledyne Isco stainless steel pump. The Teledyne Isco pump is best when any pressure will be applied to the system through the back pressure regulator. If using the Isco Pump, keep upstream and downstream valve vertical while setting it up.
6. Setup the Teledyne Isco pump using 'GRAD PROG' button on left hand side of controller. Use constant flow rate option (3?) and hit continue. It asks for maximum flow rate—type that in. It's easiest if you pick something that makes the math easier like .010 mL/min or 0.100 ml/min. For each step in the program, you must specify the starting flowrate as a percentage of the maximum, the final flow rate, and the length of time to get from initial to final for that step. To keep constant flowrate, type the same percentage in for first and final, then specify the length of time. To switch from one flowrate to the next, specify the final and then make the time 0.1 min (it's the shortest the pump can handle). Insert and delete steps as needed. If you type something incorrectly, use 'Clear Entry' not 'Delete'. 'Delete' deletes the step. Store the program. Switch to 'CONST PRESS' mode as the pump needs to start at the same pressure as the reactor for flow to begin. Set the pressure to a few hundred kPa higher than the starting reactor pressure. Close 1/8" 2-way valve used for filling. Turn downstream valve vertical to 'close' the valve. Hit 'Run' let it pressure increase. Hit 'Stop'. Go back to the gradient program menu and open your program that you've set up. Hit 'Run'. Turn valve to the right towards the injection port.
7. Check that you're on the reactor (if you want reactor measurements, else bypass) with bypass valves. Check the temperature of imbedded thermocouple and adjust furnace setpoints as needed using the up and down arrows on the controllers.
8. Now everything should be set to begin recording data
9. Setup a sequence on the Chemstation (Sequence>Sequence Table> add desired number of methods with corresponding method name—don't exceed 99 injections unless you want to change the Excel Import Sheet. Run the sequence. Once the first injection is taken (valve switches twice, once to start injection onto the columns, the second at 10s to stop injecting, do this after the 2nd switch) restart the LabVIEW program and hit 'Run' again on the pump. This times the injections properly so the flowrates and pressures will change to the next condition just after an injection giving the system an extra ~15 min to equilibrate. Congratulations, your experiment is running!

Tips for during the experiment

1. Keep an eye on the temperature as it will fluctuate with flowrates and conversion. If one or more of the zones is fluctuating significantly and has trouble staying at the setpoint, open EZ-ZONE and go to that particular controller. Setup>Control Loop> Adjust PID values to be 14 Proportional gain, 40 Integral time, 7 derivative. You can monitor the temperature remotely by using TeamViewer and the webcam on the Controller computer.
2. Always start/restart LabVIEW and pump together so the timing of flowrate changes match.
3. Also watch the pressure on the pump. If it climbs steady over time when the system pressure is not changing, the inlet is clogged. Stop the experiment and perform maintenance. If it oscillates up and down, you might have a bubble in the pump. Stop the experiment, flow at 1ml/min out into the small beaker for

10 min. Tap the sides to move any bubbles to the top of the pump. Switch flow out to the Nalgene bottle for 10 min.

4. Process data during the experiment to see if you're in the correct conversion region (0.5-10%) and that the data makes sense. This will help you determine if you need to go back and take points over or if you can speed up conditions.

Ending experiments

1. Stop GC sequence
2. Stop flow on pump and turn 1/16" valve to left to release pressure in pump.
3. Reduce H₂ flow rate to 20 sccm.
4. Switch to bypass.
5. Leave furnace and variacs on.
6. Leave system pressurized. If you constantly pressurize and depressurize you go through N₂ faster.

Shutdown Procedure [for planned power outage and leaving for extended periods]

1. Turn 1/16" valve to purge (facing left) and turn off syringe pump using 'Stop'
2. Turn bypass valves so H₂ runs through the bypass.
3. Stop Sequence on GC by selecting Abort located in the menu bar of ChemStation.
4. Exit ChemStation.
5. Turn off power to GC using the button located on the bottom left-hand corner of the front.
6. Close all valves below keyboard panel for (Air, He, H₂)
7. Depressurize system by using Labview code. Remember : up to 200 psi decrements. Cycle ball valves in system to make sure the pressure in all of the lines has been released. Close valve after system pressure is released.
8. Close main valve on N₂ and H₂ and He for the system. Currently, all the lines are shared so ask before closing the main valves.
9. Use hand pull relief valve on H₂ to release the pressure. For N₂, turn the 3 way valve on the wall just after the tank.
10. Set MFCs to 0.
11. Turn off outputs to Furnace and turn power switch to off.
12. Turn off power strips to Variacs and power strip used for MFC, pump, thermocouples. (Total of 3 power strips)
13. Unplug furnace and GC to avoid power surge.
14. Shutdown LabVIEW and any other program, and shutdown both computers.

Section 4: Waste Disposal/Cleanup

Liquid waste from the pump should be disposed of in the Organic Waste container. Be sure to include all of the components on the side of the waste container. Gloves should be worn when handling the liquid and should be kept in a fume whenever it is in an open container.

Solid waste (catalyst) that is not stored for end of life testing should be disposed of in the Solid Waste container. Label the side of the container with the catalyst composition.

Section 5: Emergency Response

Power is lost

- Close N2 tank near south door
- Close H2 tank near office door
- Turn off main power switch to furnace (switch on right)
- Turn off GC main power (button on lower left)
- Call F&S
- Call Claudia

Pressure relief valves burst

- Reduce delivery pressure on N2 and H2 tanks (near south door and office door)
- Ensure that the gas has an exit route out of the system (not blocked with 3 way valves)
- Call Claudia

Fire in hood

- Inform everyone to move to safety
- Call 911
- Follow fire safety procedures using fire extinguisher if possible or exit to safety.
- Call Claudia

- Only as long as you feel safe, turn off main tank valves for...

- Tanks near office door (2 H₂, O₂ mixtures, H₂ mixtures, and He tank)
- Tanks for GCs (H₂)
- Tanks in gas cabinet (CO/H₂, NH₃)
- Tanks near south door (N₂, He)

Section 6: Additional InformationAdvice:

Liquid inlet is fairly stable, but could still have problems. Keep 1/16" PEEK tubing, 1/16" stainless steel ferrules, and relevant fittings on hand. Keep watch for disappearing peaks on the FID indicating no flow or oscillating flow.

Start temperature dependence experiments at the lowest temperature then increase. It will go faster between measurements and you'll avoid deactivating your catalyst as quickly.

Start H₂ dependence experiments at the highest pressure and move down. This avoids a back log of flow that occurs when the pressure increases in large steps.

Keep liquid inlet at RT whenever possible based on vapor pressure of the reactants. When going to higher oxygenate pressures, increase inlet temperature. Take bypass measurements frequently to ensure that the oxygenate pressure is what is intended and no pooling is happening in the lines.

Recalibrate electronic pressure regulator every 1-2 months or when you see the pressure drift away from the setpoints (use the digital pressure gauge to check the system pressure, run through bypass at low flowrates to ensure a pressure drop in the system is not induced). Use NI Max program to send voltage to the DAQ board plot pressure vs. voltage.

Back pressure regulator diaphragm cannot be heated above 200°C. Overheating will lead to swelling of the material and misleading pressure drops. The diaphragm should be replaced every 1-2 years—keep a spare on hand.

Checklist:

- Read (Material) Safety Data Sheets.
- Proper fire extinguisher is nearby.
- Alarms have batteries and are operational
- Gas tanks have enough pressure for all conditions
- Gas tanks and lines are on and open (for necessary gases)
- All 3 way valves are properly positioned
- Line temperatures are hot enough (or cool enough at the inlet)
- All calculations are done prior to beginning the procedure.
- Pump and LabVIEW programs are set
- Temperature is set
- GC sequence is ready
- GC tanks have enough pressure

References:

Gas phase ester reduction binder (bottom left hand drawer of Claudia's desk)

Teledyne Isco D-Series Pumps Installation and Operation Guide binder (bottom left hand drawer of Claudia's desk)

Details of installation and manuals. Y:\DWF Group\CEB\Dow\System modification\Installation

DWF Group> MEW Research > Administrative and Manuals>

EZ-Zone PM Users

DWF Group> Wiki>Manuals

