Alcohol Coupling System

Standard Operating Procedure

Lab: Davenport 270

Department: Chemical and Biomolecular Engineering

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**Section 1: Overview**

Type of SOP: [x] Process [ ] Hazardous Material [ ] Hazardous Class of Materials [x] Equipment

Synopsis:

*The purpose of this SOP is to provide guidelines and safety procedures for the Alcohol Coupling 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 |
| Nitrogen | Asphixiant especially at high pressures |
| Helium | Asphixiant especially at high pressures |
| Ethanol | Flammable, eye/skin irritation |
| Acetaldehyde | Flammable, eye damage/irritation, respiratory tract irritation |

Relevant References for Material Hazards:

|  |
| --- |
| Hydrogen—Airgas,<http://airgas.com/msds/001026.pdf>Helium<https://www.airgas.com/msds/001025.pdf>Nitrogen<https://www.airgas.com/msds/001040.pdf>Ethanol<https://www.airgas.com/msds/001114.pdf>Acetaldehyde:https://www.fishersci.com/shop/msdsproxy?productName=AC175290050&productDes |

Equipment Hazards:

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

AVS 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

Legato Syringe pump—electric shock

Variacs and heating tape—Ignition source, electric shock

Glass Syringe needles—Sharps hazard

Hazardous Conditions:

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 much be worn when operating equipment for explosion and splash hazards.

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

Engineering Controls

Fume hood sashes should remain closed whenever possible, especially when flowing toxic gases.

Exit gases from system are piped up into the fume hood ventilation to reduce probability of inhalation.

Pressure relief vales should be set on all gas lines. Hydrogen and nitrogen high pressure gas lines should be set for 900 psig. GC gas lines should be set for 100 psig. He line near south door should be set for ~250 psig.

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

**Section 3: Procedures**

Startup Procedure

1. 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.
2. 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.
3. Main sure GC gas lines are pressurized to ~80psig. Open GC gas valves on hood panel (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.
4. 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 MEW Reactor LabVIEW program on Controller computer (should have a shortcut on the desktop). Check communication ports for furnace, DAQ board, MFCs, TC reader all on TPR computer. Follow directions in top of LabVIEW Front panel for instructions to set up program.
5. Close bellows 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 Hydrogenolysis and Direct Synthesis reactor as this line is shared. Open N2 valve on hood panel.
6. Close H2 valve on hood panel (labeled as high pressure H2). Open main valve on H2 tank (right most tank on rack near office door). Set delivery pressure to < 800 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 and open valve on hood panel for H2.
7. Turn on output switches to furnace and set desired temperature. It will start ramping as soon as you set it at 3 C/min.
8. System is now ready for normal operation. Use LabVIEW program to control flow rates and pressure. Program pump directly. Control temperature directly or through EZ Zone program.

Reloading Reactor Procedure

1. Stop GC sequence using Abort>Abort. Switch to Shutdown method (conserves gases and reduces power use) on dropdown method box. No need to run method.
2. Turn 1/16” 3 way valve near liquid inlet (valve A) to the left letting the pump depressurize. Liquid will squirt into small beaker. Stop program on pump.
3. Depressurize system—close H2 and N2 valves on hood panel. Open N2 bellows valve—careful, you’re releasing ~50 atm, open slowly but make sure you open it completely. Leave it open so no pressure builds in system. The system pressure will all be released at this time hissing loudly as it exits to the top of the hood. Cycle bypass 3-way valves (B and C) so there is not pressure in either the reactor or bypass.
4. Turn H2 flow to ~20 sccm on MFC keep flowing through bypass while you remove the reactor.
5. Turn off output switches on furnace. 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.
6. Unplug thermocouple from top of reactor.
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 ¼”- 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. Detach the reactor from the system at the ¼”-1/8” unions (on the ¼” 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!
9. Throw out the used VCR gaskets. These can be saved for 1 or 2 reuses. Remove the glass tube around the thermocouple and glass rod from the bottom of the reactor—set aside to clean later.
10. 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.
11. 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, and unloading date.
12. Use ¼” SS ram rod to push out remaining glass wool and catalyst. Push from bottom, out the top of the reactor. Kimwipe work station comes in handy as you’re able to wrap this up and trash it.
13. Clean reactor with DI water followed by acetone (to dry faster). Make sure all debris is removed from reactor by looking straight through it. Dry with House 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 ¼” compression fitting) in similar fashion. For top set of fittings with thermocouple, douse a Kimwipe with acetone and wipe down thermocouple and male VCR face. Clean the ram-rod, but avoid wiping off the sharpie mark ~15” from one end—this is used to determine height of the catalyst bed.
14. Slide glass rod into bottom of reactor (top is marked with an engraved T). Use new fritted VCR gasket and finger tighten bottom VCR fittings together. Ball up glass wool ~1/4” diameter and shove into top of reactor. Use ram-rod to force ball into reactor. Repeat until sharpie line on ram rod is *just* above top of reactor. Tap ram-rod to make sure glass wool bed firm and padded down. Recheck sharpie 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.
15. Add 500 mg catalyst material. If desired catalyst mass is < 500 mg, add dry Davisil 646 silica gel to the desired mass of catalyst until the total mass is 500 mg. Carefully mix the catalyst and the silica in a weigh boat prior to adding to reactor.
16. 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. Attach back to reactor at ¼” -1/8” unions.
17. Leak test first! Send the gas through the reactor turning B to right but turn C towards bypass (away from you). Gas will not be able to flow and pressure will build up. Open H2 valve on hood panel. Turn 3-way valves just upstream and downstream of 2nd MFC (the H2 only MFC) down towards needle valve. Open and close needle valve *quickly* and then *close immediately*. Pressure should increase immediately (look at digital pressure gauge) to the H2 delivery pressure. Leak rate should be < 1 psi/min. Check ¼” compression fittings at which you removed the reactor. Careful to not get soapy water 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 swageloked those fittings initially.
18. After leak checking, set the system up to do an in situ pretreatment. [Currently I use 50 sccm H2 at 1 atm] Release the pressure in the reactor (Careful!) by turning C towards the reactor. Switch 3-way valves on either side of the H2 MFC up towards MFC.
19. 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 (COM 7 currently). 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!*
20. While catalyst is pretreating, calibrate H2 MFC using bubble meter. 3-way valve near bubble meter must be pointed to bubble meter. Make sure PH3 detector is on and near you when pretreating metal phosphides. PH3 won’t be created until higher temperatures are achieved, but better to be safe.
21. At end of calibration, switch back to desired flowrate on MFC and turn 3-way valve near bubble meter back to the exhaust tubing. Update Calculation for system flowrates Excel Sheet with current MFC calibration.
22. Rewrap the heating tape and insulation on top and bottom of reactor.
23. If needed, refill pump. Fill Nalgene bottle with reactant in a fume hood. The max syringe volume is 500 mL so estimate accordingly. Cap the bottle and move to hydrogenolysis hood. Unscrew cap to slip onto 1/8” line inlet. Recap and make sure 1/8” line is at bottom of bottle. Close
24. 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. Sheet outlines guidelines.
2. System is currently set to flow H2 and He concurrently.
3. Setup LabVIEW program specifying total pressure and MFC flow rates for each data point interval. Number of injections per condition varies on experiment but is typically 3-5. Labview will do the math for you (type in injection length, and number of injections). Start the LabVIEW program and stop after ~30s allowing pressure and gas flowrates to stabilize while you setup the syringe pump.
4. There are 2 possible pumps to use—the Teledyne Isco stainless steel pump or the Legato Syringe pump. The Teledyne Isco pump is best when any pressure will be applied to the system through the back pressure regulator. The Legato syringe pump, which can sit on the removable shelf, is best when switching reactant mixtures often. The Legato is limited by the amount of force it can apply (and by the strength of the glass syringes used), reactant pressures can be manipulated by changing the amount of He flowing in the system rather than the total pressure of the system. Each pump currently has a separate 1/16” three way valve just downstream prior to where the liquid inlet meets the gas flow. The Teledyne Isco pump valve is marked A, the Legato pump valve has no label, but has the Lur-lock needle attached to it. If using the Isco Pump, keep valve A verticle while setting it up. For the Legato pump, keep the valve pointed away from the system (basically purging the pump to the open air).
5. 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. Turn 1/8” 3 way valve used for filling is turned toward the front of the hood (not towards the pump). Turn valve A 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 A to the right towards the injection port.
6. Set the Legato syringe pump using ‘Config’ button, select a listed program. If you haven’t previously made one that is useful to edit (has similar syringe size and setpoint times), create a new program. Select the syringe (Manufacturer and Size)—most common brands and sizes are listed. If not create a custom syringe with accurate inner diameter. Add steps by specifying flow rates and length of time. Check your units. Fill your syringe, make sure there are no bubbles. Attach lur-lock needle with swaged 1/16” end to the syringe and place on Legato pump by securing the syringe barrel and the barrel flange appropriately. Push the pump carriage to the end of the plunger. Using the ‘Infuse only’ mode, flow ~100 uL/min for 2 min to make sure the needle and 1/16” line is fully flushed with reactant mixture. You should keep some paper towels just at the exit of the 1/16” three way valve to catch the liquid that emerges. Once you see liquid, stop the constant flow. Switch to the program that you’ve just created. Select ‘Run’ and turn the 1/16” valve to flow towards the injection port.
7. Check that you’re on the reactor (if you want reactor measurements, else bypass) with valves B and C. 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. Make the last injection Shutdown to avoid waste) Run the sequence. Once the first injection is taken (valve switches twice, once to start injection onto the columns, the second at 30s to stop injecting, do this after the 2nd switch) restart the LabVIEW program and hit ‘Run’ again on the pump. (For the Legato pump, hit ‘Reset’ to reset the timing). 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 ~42 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. Double check flowrates on the CM-400 match the certain LabVIEW output. Occasionally the LabVIEW program messes up the string it sends to the CM-400, typically off by a decimal point. If the LabVIEW has issues, you’ll have to adjust the array of flowrates and pressures to catch the program up with where you are as well as adjust the pump program. 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. Put GC in shutdown mode.
2. Stop flow on pump and turn valve A to left to release pressure in pump.
3. Reduce He flow rate to 20 sccm.
4. Stop H2 flow rate.
5. Switch to bypass.
6. Leave furnace and variacs on.
7. 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 valve A 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. Run Shutdown mode using ChemStation by selecting Shutdown.M on the Methods dropdown menu.
5. Exit ChemStation.
6. Turn off power to GC using the button located on the bottom left-hand corner of the front.
7. Close all valves on side panel for (H2 high pressure, N2, NH3, He Process, Air, He, He and GC-H2)
8. Open N2 bellows valve under electronics shelf to release the pressure of the system. 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.
9. Close main valve on N2 and H2.
10. 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.
11. Set MFCs to 0.
12. Turn off outputs to Furnace and turn power switch to off.
13. Turn off power strips to Variacs and power strip used for MFC, pump, thermocouples, pressure gauge. (Total of 3 power strips)
14. Unplug furnace and GC to avoid power surge.
15. 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 Yao

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 Yao

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 Yao

• 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 Information**

Advice:

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. Update LabVIEW program with calibration for input and output from electronic pressure regulator.

Back pressure regulator diaphragm cannot be heated above 100oC. 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.

When using the Legato pump and changing mixtures frequently, ensure the liquid inlet is completely flushed with the new mixture. Before the removing the previous syringe, stop the gas flow, and pull the plunger to suck out and remaining liquid in the inlet. Turn the 3 way valve to the open air. After replacing the syringe/mixture, flush the needle first, then flow at ‘high rates’ into the system while flowing the gas through the bypass for ~1 min. Take a few bypass measurements to double check composition of the mixture before beginning a full experiment.

Checklist:

[ ]  Read (Material) Safety Data Sheets.

[ ]  Proper fire extinguisher is nearby.

[ ]  Alarms hare 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

[ ]  Hood sash is closed

[ ]  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:

GC installation and setup for software begins MEW#2 P.59

SS reactor assembly MEW#2 P.32-36

Liquid Inlet Redesign MEW#3 P.83-86

DWF Group> MEW Research > Administrative and Manuals>

Haysep Q Installation

EZ-Zone PM Users

D-series Pump Manual [Paper copy in lab bench drawer]

ProportionAir High-Pressure-Regulator-Installation-Guide

 GC Colum Example Chromatograms

DWF Group> MEW Research>GC Results>Integrating My Results in ChemStation\_121008

DWF Group> Wiki>Manuals

**Training Documentation**

Signing this document means that you have read and understand all aspects of this Standard Operating Procedure.

The supervisor is the person that acknowledges you took the training and understand the procedure. They can be a lab manager or researcher assigned by the PI to oversee this particular SOP.

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| **Name (Printed)** | **Name (Signed)** | **Supervisor** | **Date** |
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