IL SYNTHESIS WITH BIG REACTOR

Operating instructions

REV No.	DATE	DESCRIPTION	EDITED	CHD.	APPD.
1.0	20.2.2020	Initial version	SRa		
1.1	25.1.2023	Common problems added	SRa		

Ionic Liquid Synthesis using the 6 L reactor

The six litre reactor (Figure 1) used to synthesize ionic liquid (IL) is located in the CHEMArts lab, in the Aalto Bioproduct Centre (A!Bio). The setup is in a ventilated compartment behind folding safety doors in the furthest corner. The reactor vessel has a five-neck lid and a temperature-controlled jacket. The setup is equipped with speed adjustable agitator, a peristaltic pump and a thermometer. There is also the possibility to use an external nitrogen supply.

Figure 1 – Reactor setup

Safety

You should always plan your work before starting and go through all the safety issues involved. Read through the material safety datasheets (MSDS) and use according safety equipment and procedures.

Read carefully through the instructions. If something is left unclear, always ask for further instructions. You are responsible for the safety of yourself, the equipment and others in the vicinity.

The synthesis process involves highly corrosive chemicals and they should be handled with care. Be careful of chemical residues before and after the process. Clean and dry the parts thoroughly after your work!

Preparations

In the synthesis process an equimolar amount of acid will be added to the base. Using the amount of base as a starting point we can calculate the amount of acid needed:

$$m_{Acid} = m_{Base} * \frac{Mwt_{Acid}}{Mwt_{Base}} \quad (1)$$

Start by making an estimate of the amount of chemicals to reserve for the synthesis using the equation and the properties of the used chemicals (see the table below AND **see for changes in the chemical containers!**). Make sure the reactor will capacitate the total amount of chemicals, but also that the initial amount of base is enough to cover the stirring blade.

Table 1- Chemical properties

Chemical	*M* [g·mol^{-1}]	*n* [mol]	*m* [g]	*mass fraction*	*density* [g·cm^{-3}]
DBN	124.187	1	124.187	0.674	1.005
Acetic acid	60.05	1	60.05	0.326	1.049

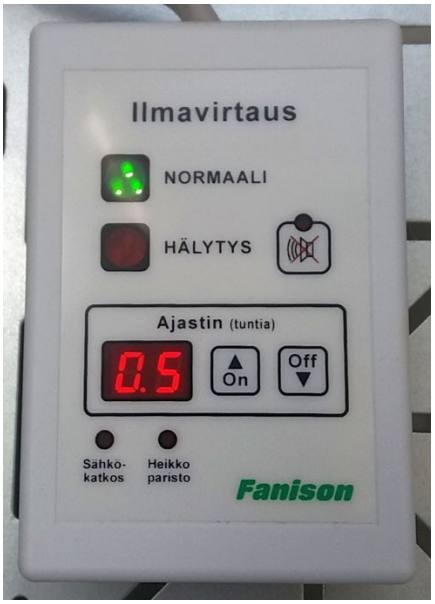
In addition to the needed amount of chemicals, you should have

- proper safety equipment
- a funnel for pouring liquids (at the reactor)
- special bottle cap for pumping the acid (at the reactor)
- a plastic measuring jug (at the reactor)
- Duran® bottles for storing the ionic liquid

- optional: smaller sample bottles (NMR, EC, KF…)
- optional: pre-printed labels for bottles

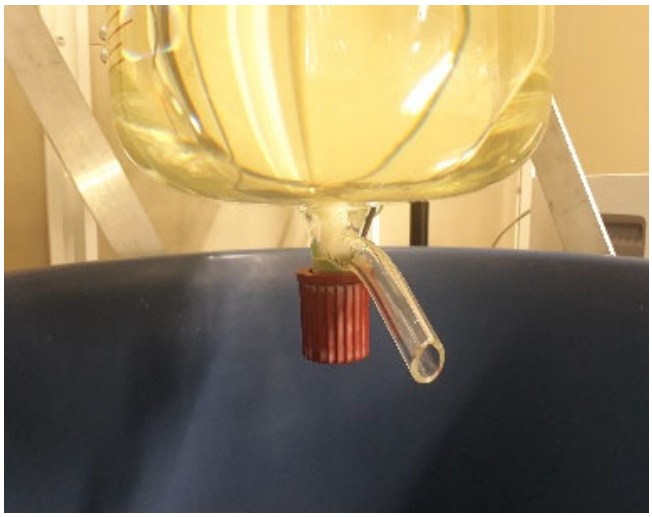
If for some reason there is still moisture inside the reactor when you are starting, dry it as described in Cleaning up. Turn on the fume ventilation - the control panel (see Figure 2) is located at the far end of the compartment away from the reactor. Set it for at least 2.5 hours by pushing *On* multiple times. Also switch the lights on from the adjacent white switch.

Figure 2 – Ventilation control panel



The scale is located next to the reactor - **level and calibrate it**. Double check that the outlet valve at the bottom of the reactor is closed! Also make sure that the top blue ventilating valve is closed (vertical is open, horizontal is closed). (See Figure 3)

Figure 3 – Reactor outlet valve and ventilation valve



Bottom outlet valve

Top ventilation valve (in open position)

Synthesis

Use the funnel to help pouring the base into the reactor. Weigh the total amount of base added and write it down. You can calculate the exact amount of base added into the reactor with equation:

$$m_{BASE} = m_{full\ bottle\ before\ addition} - m_{empty\ bottle\ after\ addition} \quad (2)$$

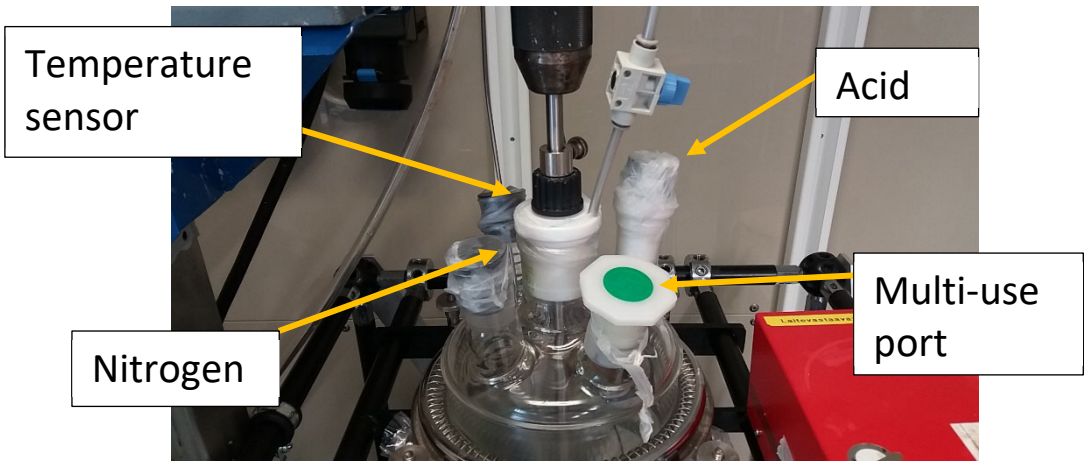
Now that you know the final amount of base inside the reactor, you can calculate the exact amount of acetic acid to be added using equation 1. Different tests, such as nuclear magnetic resonance (NMR), can be run on the final product to evaluate and alter the acid-base-ratio.

If need be, follow the instructions on *Nitrogen flushing*. Otherwise continue with the normal procedure.

Figure 4 - Acid bottle with the special cap and its connectors

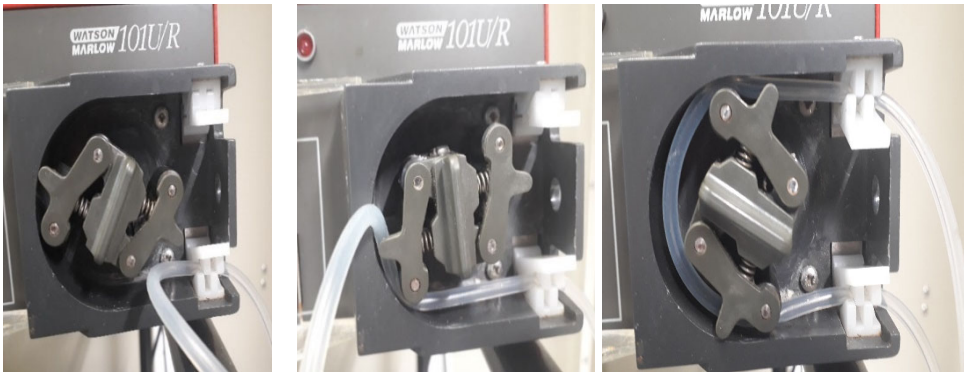
If you are using a new bottle of acid, write down the opening date on the bottle with a permanent marker, preferably with a ballpoint pen. Place the bottle on the scale and change the cap to the special one with the tubes and connectors (See Figure 4 for assembly and attachment). Make sure that the thin tube reaches the bottom part of the bottle to ensure continuous flow.

Figure 5 - Reactor vessel ports



Insert the pressure balancing stopper, at the end of the thicker tubing, in to the multi-use port (see Figure 5). Next run the thin tube through the pump mechanism (see Figure 6) and the acid inlet stopper. Position the end of the tube inside the reactor in such a way that the acid will not run along the container sides but drip into the base.

Figure 6 - Installing the tube in the pump



Steps how to secure the tube in the pump: 1. Secure in the white clasp 2. Turn the pump clockwise and 3. Secure with the upper white clasp again. Be sure you have the right direction!

Figure 7 - Pump settings

Initially the pump can be set to the highest speed, 99, using the push buttons. Other settings usually should not be used or changed, but you can check that the pumping action conforms to the bottom to top tube arrangement and pumping is set to manual, as seen in Figure 7.

The stirring mechanism is controlled from the controller box located in the left bottom part of the reactor (Figure 8). You control the speed with the black knob (turning it counterclockwise slows down), the red switch is the main power switch. Start off with a lower speed and gradually turn it to maximum speed.

Figure 8 - Stirrer controller box

At this point make sure all the reactor port stoppers are in place. Check the connections are secure and ONLY if need be, seal with Parafilm. Start the stirring mechanism.

Next, power up the reactor jacket temperature control unit located on the right side of the reactor. The main unit with the pump and water reservoir is below, the small thermostat (See Figure 9) sits on top of it. Both main and control unit have a mains switch located behind them.

Figure 9 - Thermostat

Push the power on/off button on the thermostat to turn it on. Use the arrows to move the cursor in the interface and middle button to operate/activate. Use the interface to set the temperature accordingly (70 °C normally) and turn the pump on. Be aware that the run/stop symbol shows the function, not the current status.

Figure 10 - Thermometer

The heat from the heating jacket ensures the ionic liquid will not crystallize, but the exothermic reaction will also give off heat. Use the thermometer (Figure 10) to monitor the temperature of the liquid during the synthesis process. Temperature should not reach over 90 °C.

To ensure you measure the actual amount of added acid in the end: Start the peristaltic pump and stop it the moment the acid has reached the end of the tube inside the reactor. When stopped the system is

more stable for taring. Tare the scale, and then restart the pump to start the synthesis process.

Depending on the total amount of acid to be added, it will take around 1-1.5 hours to finish this part. One gram of acid takes around five seconds to be pumped at the maximum speed.

Leave a note with your full name, phone number and the total amount of acid to be added. If something goes wrong, you can be contacted, and you can ask someone to stop the pump if you are not able to yourself. Close the safety doors.

Occasionally check the thermometer, which you need to turn on occasionally. You may adjust the jacket temperature or the pumping speed, if the temperature starts to approach the upper or lower limits. These changes though do take time to have effect.

When almost all the acetic acid has been added start reducing the speed of the pump. Stop the pump when the final amount has been reached. If it differs from the calculated value, write it down.

It is convenient to have the plastic jug to place in all the tubes and other parts for the next stage. Replace the acid inlet stopper with a regular one, to prevent extra acid being added.

Take out the tube from the pump mechanism. Next remove the pressure balancing stopper and replace it with a regular one. Replace the special acid bottle cap with the original. If acid was left in the bottle, recheck it has an opening date.

Let the stirrer run for another 15-30 minutes and then turn it off. You can use that time for example to clean the funnel, acidic parts and tubes (See

Cleaning up).

The bottom outlet valve will be used to bottle the ionic liquid into glass Schott bottles, that can withstand heating. Keep in mind the liquid will still be hot at this point. If there would be a slight vacuum inside the reactor, preventing the liquid flowing freely from the open valve, slightly opening one of the stoppers releases the pressure.

More than often one litre bottles are used and not filled totally full (no more than 80%). Repeated heating will have deteriorating effects on the ionic liquid, so aim for such amounts you can use on one go. For example, two bottles with around 750 g of ionic liquid each might be ideal for preparing a dope for the large spinning machine.

It might be easier to take possible samples (for NMR, CE, etc.) straight from the reactor outlet valve. Parafilm may be used for extra sealing, if the bottles would be stored for prolonged periods. Samples are stored in Room 261, in cabinet A3 (See laboratory map).

Cleaning up

After draining all the ionic liquid, remove all the stoppers and close the bottom outlet valve. Fill the reactor with deionized water all the way up to the vessel lid and necks. Turn the stirrer on and let it run for at least five minutes with the thermostat at 70 °C.

Slow down the stirrer to minimum and power it off. Turn off the heating jacket and thermostat, powering them off as well. You can drain the rinsing water from the reactor to the bucket beneath by opening the bottom outlet valve. The bucket itself has a drain hole.

Connect the tube from the compressed air tap to the tube connected to the top ventilation valve (See Figure 11). The bottom outlet valve should be still open to ensure air flow. Open the ventilation valve (perpendicular position) and the compressed air valve. Let the air flow until dry.

Figure 11 - Drying the reactor with compressed air

Clean and dry all the parts: stoppers, tubes and equipment used during the synthesis that have been in contact with chemicals using de-ionized water. Make sure to remove all chemical residues! **Equipment should be clean, dry and especially safe for the next user.**

You can use the movable local ventilation snorkel over the CHEMArts washing sinks if the smell of acetic acid is too much.

Don’t forget to disassemble the tube-cap-combination for pumping acid. You can use a syringe to pump de-ionized water and air through the tubes. For the thinner tube it might help to use the blue tubing at the reactor as an “adapter”. (See Figure 12) Clean and dry them after use as well.

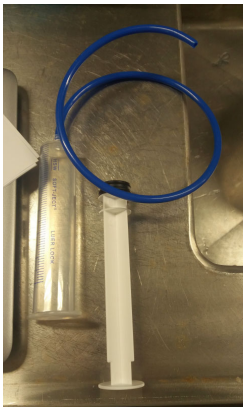


Figure 12 - Syringe adapter

The empty chemical containers (base and/or acid) should be rinsed well, marked down as being rinsed and can be disposed of as general waste.

Protocol

Fill in the required data according to protocols (e.q. Dope preparation in Spinlog). Example for the preparation of about 1800 g of [DBNH]OAc:

		1 DBN	2 Acetic acid	
Bottle (empty)	g	998.39	569.25	
Bottle + chemical	g	2219.04	1157.18	
Bottle after addition (empty)	g	1003.89	569.92	
Amount added	g	1215.15	587.26	
Addition for correction	g		0.54	**Total**
Final amount	g	1215.15	588	1803.15
mass fraction		0.6739	0.3261	
moles n	mol	9.7885	9.7795	
n difference	mol	0.0090		

Nitrogen flushing

The nitrogen supply is equipped with a flow regulator and a rotameter (see Figure 13). The first gauge (left) shows the pressure between the gauge and the bottle valve (basically the pressure inside the bottle when bottle valve is open). The outermost flow valve can be used to control the gas flow more conveniently when the bottle valve is open. The second gauge shows the outflow pressure (basically the pressure at which nitrogen flows into the reactor), which you can alter with the adjacent regulator.

Figure 13 - Nitrogen source

Insert the tube from the nitrogen supply through the rubber plug (front left) into the reactor. Close the flow valve and open the bottle valve, only few turns. The pressure inside the bottle should be high, if not, nitrogen might be running low (in that case contact technical personnel). Open the flow valve a bit and adjust the outflow pressure if necessary. Then you can open the flow valve fully to start the flushing.

After you are done with flushing, close the flow valve, remove the tube from the reactor and seal or replace the plug. Close the bottle valve as well. Clean parts of chemical residue.

Common problems and resolutions

Thermostat gives an Low Level Cutout (LLC) error

Water level in the water reservoir is below the warning limit, and the thermostat stops itself.

Figure 14 – Thermostat low water level -error

Resolution: Add water to the water reservoir

For further questions, contact:

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SYNTHESIS QUICK CHEAT SHEET

- Lights and ventilation
- Assemble acid feed tube/cap -thing
- Inspect the reactor
- Close vent and bottom valves
- Tare scale
- Measure and pour the base in to the reactor
- Calculate total acid amount to be added
- Set up the acid feed
- Start mixing
- Start heating
- Start acid feed pump

- Stop acid feed
- Let it run for a while
- Bottle the product
- Clean up!