THF Still Standard Operating Procedure

General note: All materials needed for the process outlined below (3 L RBF, heating mantle, Variac, distillation head, thermometer, bent vacuum adapter, long glass rod, etc.) is available and housed under the oven next to the rotovaps in a labeled plastic bin. Please keep all the components in a single place and return after use.

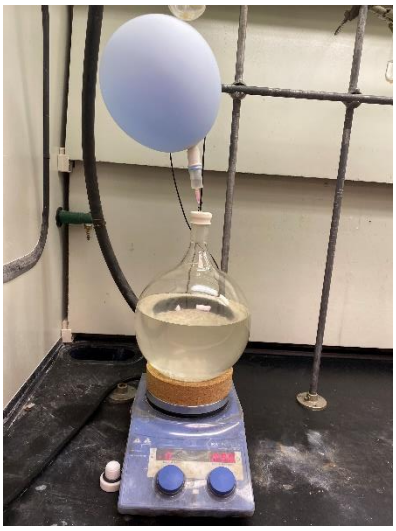

Figure 1: Pre-drying of the THF with sodium hydroxide.

Pre-drying the THF:

1) Add 2 L of THF (depending on availability this THF can be from GPC waste or can be from a fresh 4 L) to a 3 L single necked round-bottomed flask (RBF) equipped with a large magnetic football shaped stir bar.
2) To this was added ~60 grams of NaOH (30 g of NaOH/1 L of THF), the RBF was capped with a rubber septum, and the flask was equipped with an N_2 filled balloon.
3) The THF/NaOH mixture was allowed to stir (~750 rpm) at room temperature for ~16 hours (**Figure 1**).

Notes: After an extended period of stirring, especially with recycled THF from the GPC, the pre-dried THF can go pale yellow. This is fine. If you require larger volumes of THF to refill the still, this can be done in two separate 3 L single necked RBFs.

Distilling the pre-dried THF:

4) After this period, the 3 L RBF was placed into a properly sized heating mantle plugged into a Variac (*note:* this component is necessary, *do not plug the heating mantle into the wall directly*, the Variac will adjust the voltage of the alternating current [AC] so that just enough heat will be produced by the mantle to distill the THF) on top of a standard stir plate.
5) The septum was removed, a distillation head equipped with a thermometer was placed onto the RBF, a distillation condenser was attached to the male output of the distillation head, a bent vacuum adapter was placed onto the male output of the distillation condenser, and finally a 3 L RBF was placed onto the bent vacuum adapter. The ribbed 10 mm connector of the bent vacuum adapter can stay open to air, no special precautions are necessary (**Figure 2**, *top*).
6) The cold water running to the condenser was turned on, the Variac was set to 60 (**Figure 2**,

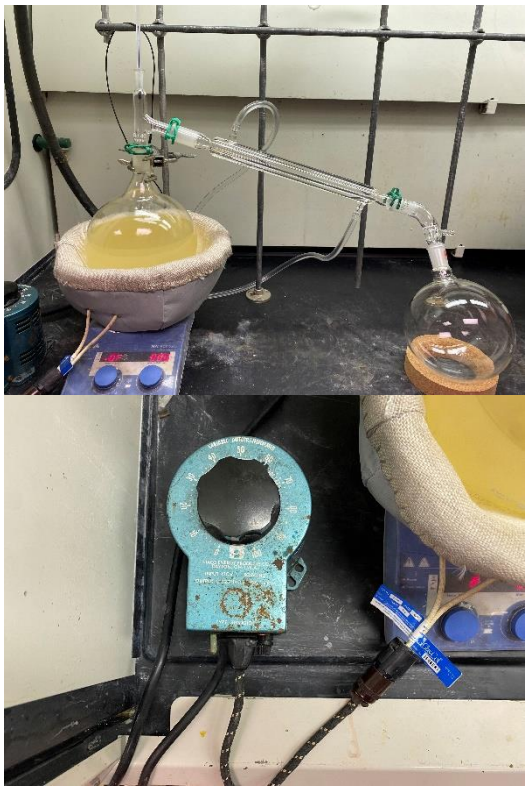

Figure 2: *Top* – Set up for distilling THF. *Bottom* – Set up for Variac (set to 60).

bottom), and the THF/NaOH mixture was stirred (~750 rpm). After 20-30 minutes, the THF should begin distilling. Allow the distillation to continue until ~100-200 mLs of a THF/NaOH slurry remain in the 3 L RBF and most of the THF has collected in the receiving flask. Add water to any remaining, non-distilled THF to form a predominately aqueous solution and place the contents into the aqueous waste.

Drying the THF with sodium metal:

7) One 200 mL beaker was placed onto the analytical balance and the weight was zeroed. An additional 200 mL beaker was filled with ~100 mL of reagent grade hexanes. Cubes of sodium metal immersed in mineral oil were extracted using long tweezers, placed into the 200 mL beaker containing hexanes to remove the mineral oil coating and then placed into the empty beaker on the balance. This process was continued until ~15 grams of sodium metal were inside of the empty beaker.
8) The beaker containing the ~15 grams of sodium metal was immersed into ~50 mLs of reagent grade hexanes to halt further oxidation of the surface.
9) The ~15 grams of sodium were cut into small pieces to expose unoxidized surfaces of the sodium using a razor blade.
10) The small pieces of cut sodium metal were placed into the distilled THF, the mixture was stirred at room temperature for ~16 hours (overnight). The reaction mixture was capped with a septum and equipped with a needle to allow evolved hydrogen gas to escape.

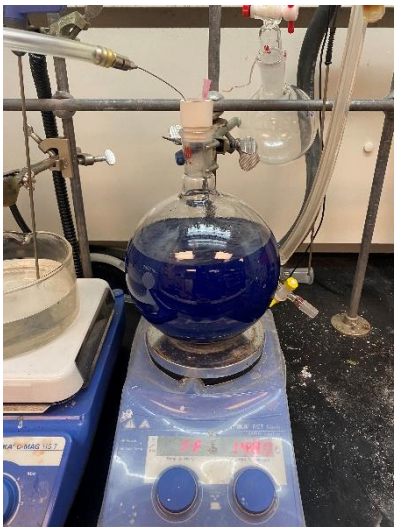

Figure 3: THF/sodium mixture after the addition of benzophenone and degassing with nitrogen.

Deoxygenating the THF with benzophenone:

11) After allowing the THF to stir with sodium for ~16 hours, it should be noted that no further gas was evolving, and the solution had become slightly opaque.
12) The THF/sodium solution was then sparged with nitrogen gas for 10 minutes with rapid stirring using a long needle. The needle was placed below the THF layer to allow the nitrogen to bubble through the solution.
13) To the degassed solution was added ~3 grams of benzophenone. If the above process was done properly, the solution should start to immediately turn blue. If not, don't freak out. Further sparge the solution with a stream of nitrogen gas for 10 minutes with rapid stirring. After this time the solution should be dark blue/purple and no further operations are required (**Figure 3**).
14) If the solution is clear or yellow (and not a dark blue), add another scoop of benzophenone (~1-2 grams) and further sparge the solution with a stream of nitrogen gas for 10 minutes with rapid stirring. Repeat this step until a dark blue solution is obtained.

Filling & maintaining the still:

15) Dismantle the still and add the dark blue solution of THF including the sodium metal chunks to the 5L RBF.
16) Reassemble the still (**Figure 4**, *left*).

Figure 4: *Left* – The fully assembled THF still ready for operation. *Right* – The flow meter with a red arrow showing the correct flow rate.

17) Adjust the nitrogen flow so that the flow meter registers at ~0.2 standard cubic feet per hour (SCFH) (**Figure 4**, *right*).

Still standard operating conditions:

The Variac attached to the heating mantel is plugged into a Christmas light timer that runs from 9 am to 12 pm. If you want dry THF, make sure that you turn the stopper to collect during that period. Do not change the time if you want THF later in the day, just switch the red switch on the side from "timer (T)" to "on" and collect the distilled THF. Make sure you remember to switch it back to timer when done collecting.

The THF still should be blue, meaning that the contents of the still are free of oxygen and water. If oxygen starts to contaminate the still the color of the THF will change. The order of increasing contamination can be tracked calorimetrically: blue (best), green, brown, yellow (worst).

Quenching the still:

After 6 months of continuous operation and several refills the still will eventually turn brown and will need to be quenched. Any remaining THF in the still should be distilled, collected, and submitted to **step 7** (above). ~200 mLs of THF should be allowed to remain in the large RBF so that it is not distilled to dryness. The remaining THF, sodium, and accumulated decomposed materials should be cooled with an ice bath prepared in a large plastic tub, stirred rapidly, and added enough MeOH to quench any remaining sodium metal (all sodium should be dissolved). The sodium methoxide solution (which is normally dark brown) can be placed into a 4 L amber bottle, labeled, and disposed through EH&S.