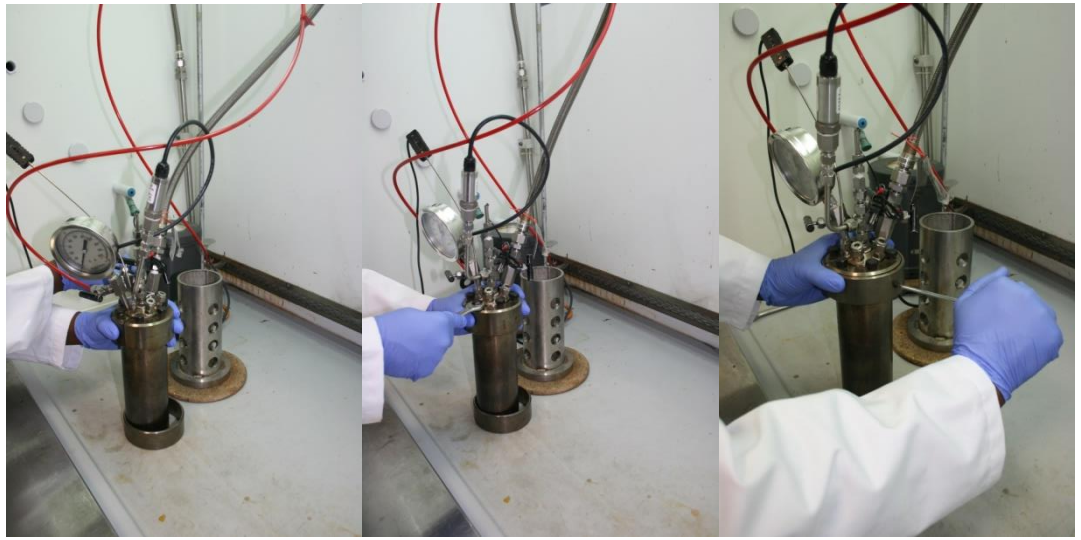
Conversion of Wet Waste to Fuel and Value-Added Products using Hydrothermal Carbonization



Laboratory scale HTC experiments

UKIERI
UK-India Education and Research Initiative

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE

UNIVERSITY OF LEEDS

Part 2- Laboratory scale HTC experiments

Session 1: Reactors and standard operating procedures

Session 2: Sample work-up and separation of products

Session 3: Health and Safety considerations

Session 1- Reactors and standard operating procedures

This session will cover:

- Types of reactors
- Preparation of feedstocks for HTC
- Setting up a HTC experiment
- Typical operating procedures
- Processing variables

Session 2- Sample work-up and separation of products

This session will cover:

- Separation and processing HTC products
- Determination of products yields
- Storing products for further analysis

Session 3- Health and Safety considerations

This session will cover:

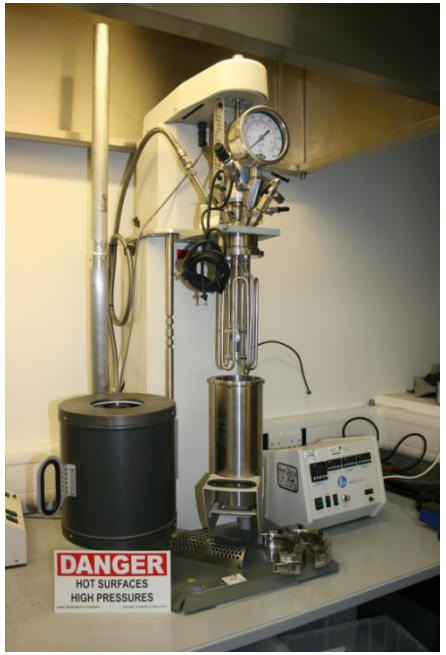
- How to operate a high pressure hydrothermal reactor safely
- Risks Associated with hydrothermal reactions
- Pressure and temperature
- MSDS of products and feedstocks

Session 1
Reactors and standard operating procedure

Types of reactor

- There are many different types of laboratory reactors used but the vast majority are batch reactors
- Batch reactors come in many shapes and sizes, they are typically externally heated using electric heaters
- Reactors typically have slow heating and cooling rates
- Typically stainless steel or Inconel high pressure reactors

Types of reactors



2 litre stirred

0.6 litre non stirred

50 ml non stirred

2 litre stirred

2 litre non strirred

Sampling mixed wastes

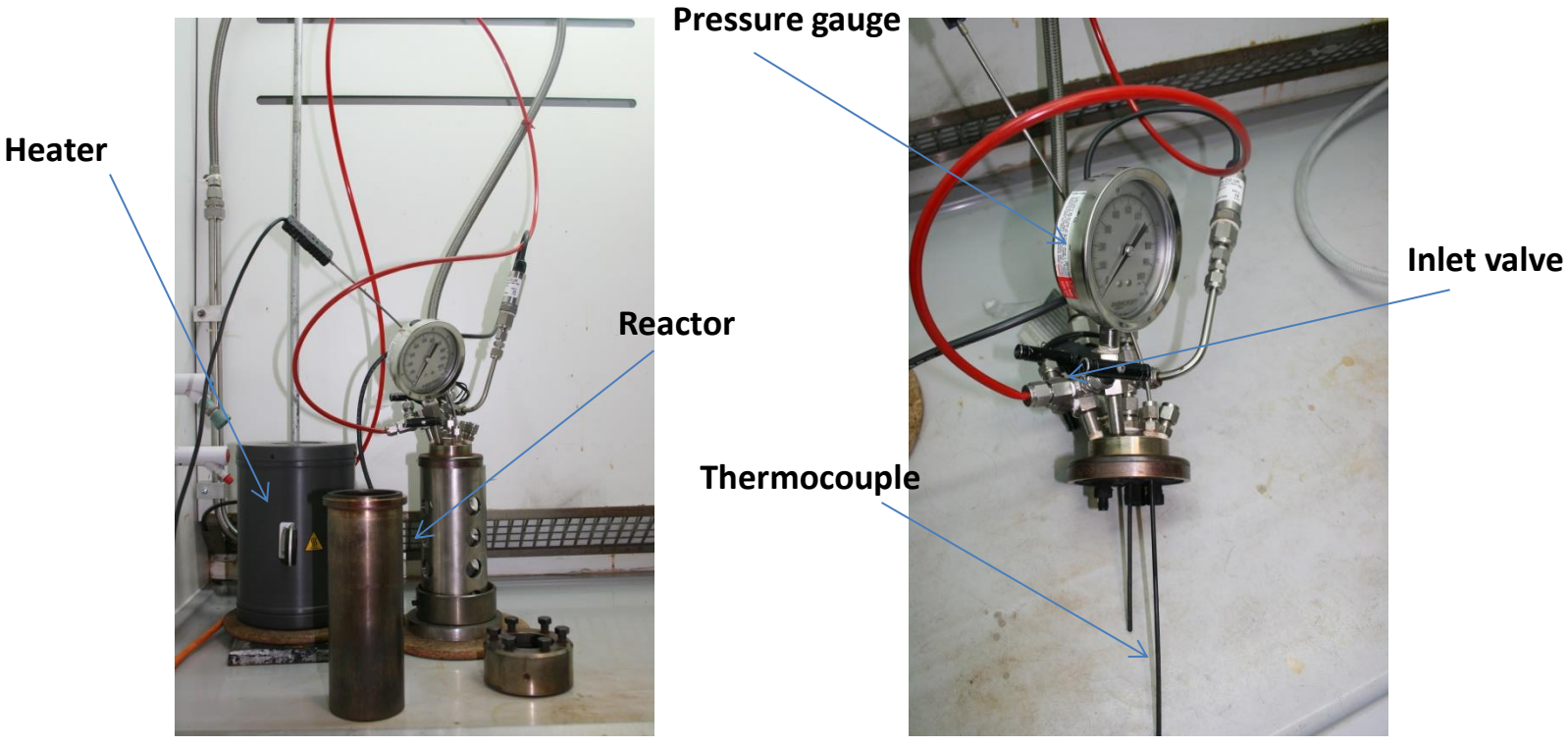
Desiccation

Homogenisation

Sample homogenisation

- When processing heterogeneous wet wastes such as food waste, important that sample is representative
- Homogenisation can be performed by size reduction and mixing
- Allows the effect of process variables to be assessed

High pressure batch reactors



High pressure batch reactors

- HTC is typically carried out using thick-walled pressure vessels.
- The pressurized vessel allows for operation at high pressure with appropriate safety concerns abated.
- The following protocol highlights the procedure for the safe operation of these high-pressure reactor vessels.

Loading feedstock into reactor

- Sample is first placed either directly into pressure vessel or into glass quartz insert- Correct amount of biomass is weighed to get specific solid loading




10-30 wt% solid loading in deionized water

Addition of additives

- Reactor is typically loaded with 10-30 wt% solids
- Additives such as mineral and organic acids sometimes added (e.g. formic acid, citric acid etc)
- Care should be taken to ensure correct materials are selected to avoid corrosion

Sealing of reactors

- Sample is loaded into reactor and is sealed by tightening the bolts in a even manner around the reactor

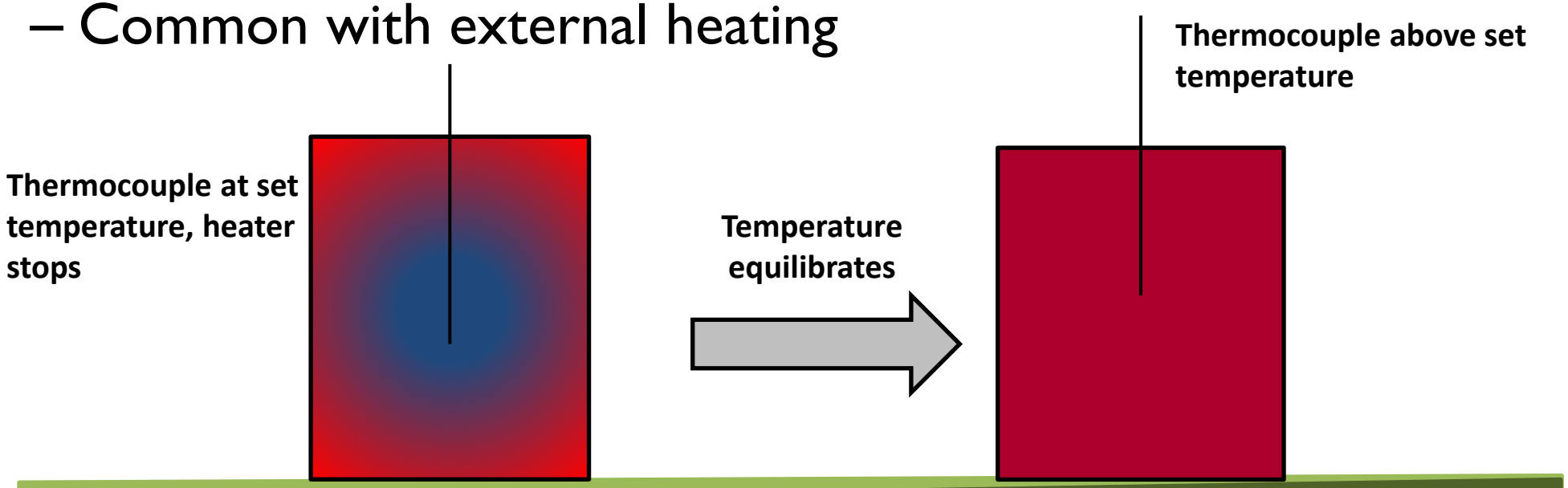
Setting temperature

- Set temperature and ensure there is a safety cut off in case the temperature increases rapidly
- PID control for the heater should be calibrated for the set temperature range to reduce potential for overshoot.

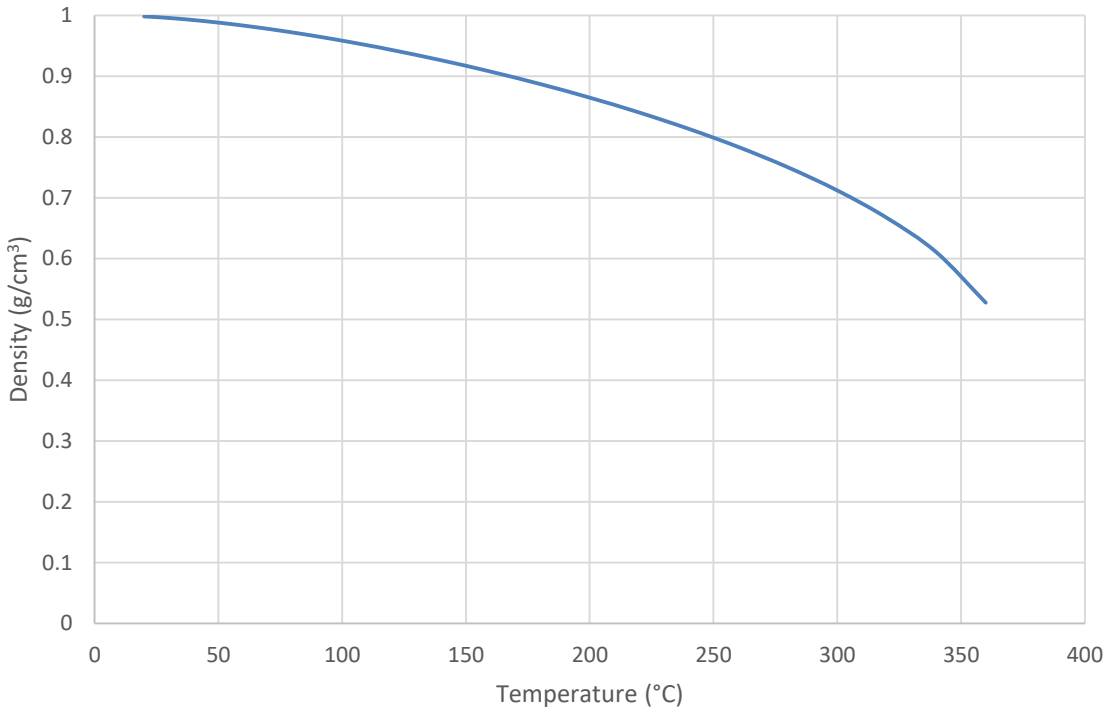
Temperature measurement

Overshooting temperature target can lead to serious failure

- Thermal gradients in the reaction vessel may lead to an underestimation of the temperature
- Common with external heating

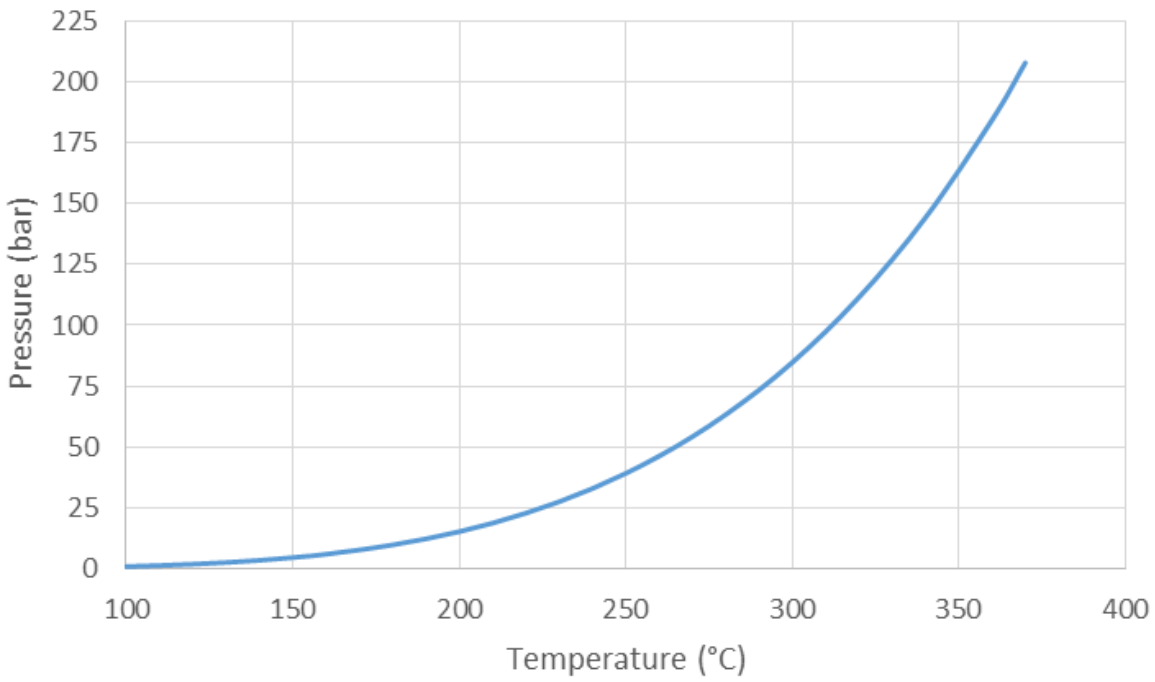


Density vs Temperature



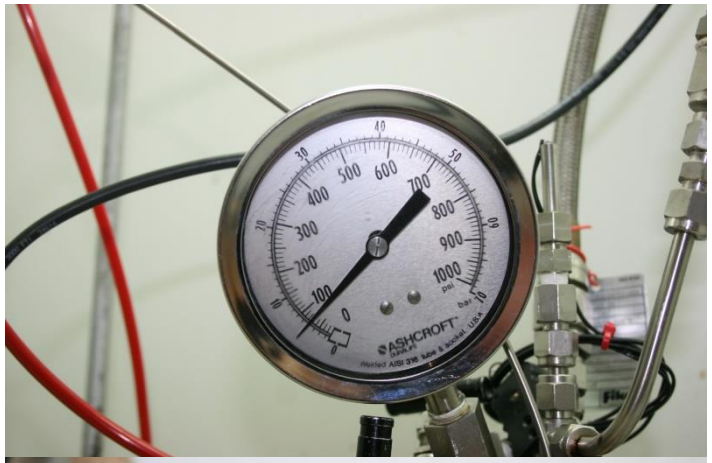
- In most situations water is considered incompressible, meaning volume and density are independent of pressure.
- However, density is dependent on temperature.
- Solid substrate used likely to be less dense than water. Takes up more volume.
- The volume in reactor will be 25% greater after heating to 250°C.
- Not accounting for expansion of liquid will result in rupture of the vessel.

Pressure temperature relationships



- Pressure rises exponentially with temperature
- Consider what temperature overshoots equate to in terms of pressure
- Would a small temperature overshoot lead to failure of vessel?
- Overshooting by 20 °C at 300°C leads to 27bar pressure rise vs. just 5bar at 150 °C

Emptying reactor



- Ensure the reactor has cooled to below 50°C before opening the reactor.
- You may need to cool down even more if the sample contains volatile species
- Note the pressure and temperature when opening the reactor.
- Vent the gas either to waste through a waste pipe or into a gas bag for sampling the gas

Question and answer session

- Thank you for listening
- Any Questions?

Session 2
Sample work-up and separation of products

Emptying reactor: Steps

- Once insert is removed from the reactor, it is weighed and then the contents filtered through a Buchner funnel
- The process water is transferred to a plastic container and hydrochar is removed and air dried
- It is then dried to constant weight in an oven to determine the mass of hydrochar

Drying and storing the products

- The hydrochar is dried in an oven at 60°C
- It is good practice to repeat sample at least in duplicate
- Process waters can be separated and placed in the freezer for storage before analysis

Determination of yields

- HTC mass yields are determined gravimetrically.

$$Hydrochar\ Yield\ (\%\mathrm{HY}) = \frac{M\mathrm{hc}(g)}{M\mathrm{b}\ (g)} \times 100$$

- Where, *M*hc is the mass of dried hydrochar (g) and *M*b is the mass of dried biomass added to the HTC reactor (g).

- The gas yields can be determined as the percentage difference between the total input and total output masses. Process water yield can be calculated by difference.

Carbon balance

- The carbon distribution in the hydrochar can be determined by:

$$\mathbf{C-distribution\ to\ Hydrochar}\ (\%) = \frac{\left(\frac{\mathbf{C\%hc}}{\mathbf{100}} \times \mathbf{Mhc}\right)}{\left(\frac{\mathbf{C\%b}}{\mathbf{100}} \times \boldsymbol{M}\mathbf{b}\right)} \times \mathbf{100}$$

- C%hc is the C-content of the hydrochar (% as received), M*hc* is the recovered mass of hydrochar (g), C%b is the C-content of the dried biomass (% as received) and M*b* is the mass of biomass added to the HTC reactions.

Carbon balance

- The carbon distribution in the process water can be determined by:

$$\mathbf{C-distribution\ to\ Process\ Water}\ (\%) = \frac{(\mathbf{TC}\boldsymbol{pw} \times \boldsymbol{Mpw})}{\left(\frac{\mathbf{C\%b}}{\mathbf{100}} \times \boldsymbol{M}\mathbf{b}\right)} \times \mathbf{100}$$

- TCpw is total carbon content of the process waters (g/L), *M*pw is the recovered mass of process water (kg), C%b is the as received C-content of the dried biomass and *M*b is the mass of biomass added to the HTC reactions. It is assumed 1 mL of process water has mass of 1 g.

Ash removal efficiency

- The ash removal efficiency from hydrochars can be calculated by

$$\textbf{Ash Removal}\ (\%) = \mathbf{100} - \frac{\mathbf{Ash\%hc}}{\mathbf{Ash\%b}} \times \mathbf{HY}$$

- Where Ash%hc represents the ash content of the hydrochar (% as received), Ash%b represents the ash content of the biomass (% as received) and HY represents the hydrochar yield.

Question and answer session

- Thank you for listening,
- Any Questions?

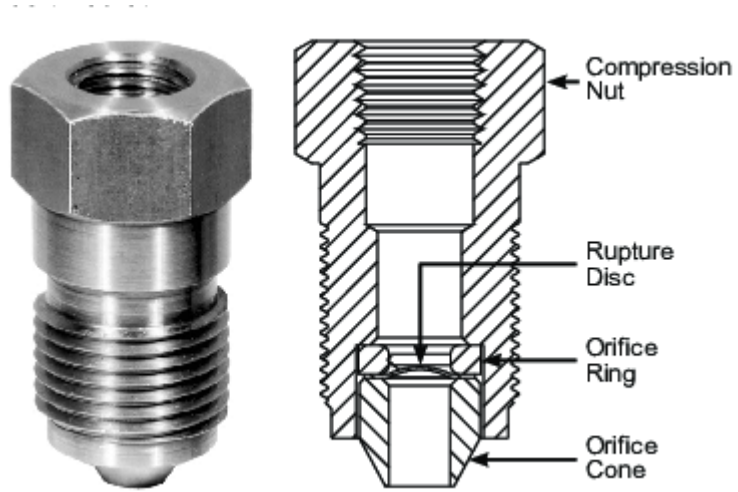
Session 3
Health and Safety considerations

Health and Safety Risks

- Operating at Higher pressure
- Operating at high pressure
- Dealing with Toxicity of products
- Dealing with Toxicity of Gases

Bursting Disk Assembly

- High pressure autoclaves should be fitted with a rupture disk assembly to avoid over pressure and explosion
- Rupture disks are designed to rupture at specific pressures and so are set for a particular reactor
- Should not exceed 90% of burst pressure. NB Burst pressure drops with temperature



Rupture Disk Failure

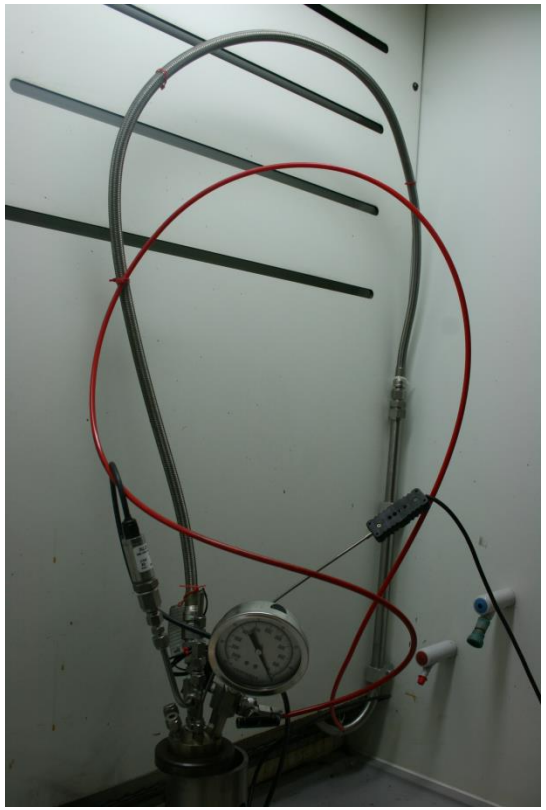
If a rupture disk were to blow, the following could occur.

- High pressure jet of hot steam
- Loud bang that could damage ears
- Large forces that suddenly act

To mitigate any risks

- Securely fasten vent in direction away from users
- Select tubes wisely, often fail at lower pressures when rapid changes occur from explosions
- Long tubing from rupture disc reduces noise
- Adequate ventilation

Containment



- The rupture disk should be connected to a fixed outlet pipe to vent the contents of the reactor if rupture disk exceeded. This needs to ensure the contents are directed away from the operator.

- The reactor and bursting disk outlet pipe should be contained in a ducted area to ensure no gases and vapours can enter the laboratory

Choosing the right reactor vessel

- Select a reactor or pressure vessel which has the capability, pressure rating, corrosion resistance and design features that are suitable for its intended use

- When a pressure vessel is delivered without a pressure relief device, it is the customer's responsibility to provide pressure relief in order to protect the operator and the equipment from destructive high pressures

- Establish training procedures to ensure that any person handling the equipment knows how to use it properly.

- Maintain the equipment in good condition and establish procedures for periodic testing to be sure the vessel remains structurally sound.

Pressure testing

- Under the Pressure Systems Safety Regulations 2000, a written scheme of examination is required for most pressure systems. Exempted systems are listed in the Regulations. Generally speaking, only very small systems are exempted.

- Remember, an examination undertaken in accordance with a written scheme of examination is like an MOT for your car. It is a statutory examination that is designed to ensure that your pressure system is 'roadworthy'. It is not a substitute for regular and routine maintenance.

Personal Protective Equipment (PPE)

Hot

Cold

Key Risks

Risks	Operator considerations	Mitigating Measures
Burns	Wear Heat Gloves	Allow to cool before opening
Chemicals	Wear PPE, operate in ventilated area	Review MSDS sheets
Electrical	Ensure equipment PAT tested	Standard SOP/Inspection
Fire	Remove flammable material	Operate away from flammable material
Rupture	Operate within pressure rating	Pressure test, inspect rupture disk

MSDS

- Feedstock- dusts , biohazards, sharps, odour
- Process waters, soluble toxic organics, heavy metals, acidic
- Hydrochar, dusts, fire risk, mould,
- Gases, combustible, potential toxics

Explosions

- Explosions in the chemistry laboratory result from reactions that liberate heat or volumes of gas or both. By working on a small scale, as we always should with unknown reactions, we minimize the chance that liberation of heat alone will lead to an explosion.
- We can then concentrate our attention on those reactions that can lead to a sudden increase in volume.

Temperature measurement

- Place thermocouple at an appropriate position
- Consider stirring to remove gradients
- Thermal gradient greater if solid loading increased or if a sludge is used
- Consider slower heating rate when close to set-point
- Use pressure transducer and pressure-temperature relationship to estimate the greatest temperature in the vessel.

Safely handling of products

- **Process waters**
  - Sterile
  - Low pH can cause irritation
  - Presence of volatile compounds, e.g. formic acid

- **Hydrochars**
  - Inhalation risk

Leaking Vessels

- Leaks onto heater can cause power to short circuit and water damage.
- Hydrochar and process water deposits can build up on parts such as valves causing them to not seal properly.
- Leaks tend to be slow and hard to spot

Leaking Vessels

- In case of an accident or unexpected overpressure,the safety rupture disc should burst to relieve the vessel before it is damaged by excess pressure. Therefore, provisions must be made to handle the noise and any potential fume hazards created by this release. Extension piping attached to the safety rupture disc fi tting and leading to an appropriate discharge area offers the best protection against this possibility.

Loading Limits (MAWL)

- One of the most frequently overlooked hazards that can arise in pressure vessel operation is overfilling the vessel.
- A vessel must never be filled to more than two-thirds of its available free space, and in some cases the charge must be reduced even further for safe operation.
- Dangerous pressures can develop suddenly when a liquid is heated in a closed vessel if the available free space is not sufficient to accommodate the expansion of the liquid.
- This is particularly true of water and water solutions which may increase to as much as three times their initial volume when heated from room temperature to the critical point at 374 °C.
- Although this problem can arise when heating any fluid, it is particularly dangerous when working with water, as shown by the data tabulated below.

Loading Limits (MAWL)

- At temperatures up to 200 °C the increase in volume is small. But as temperature is raised higher, the fluid expands to fill 150% of its original space at 321 °C, and to more than three times its original space at the 374 °C critical point.

- To prevent damage from this type of expansion, the amount of water placed in any sealed pressure vessel should not exceed the volume determined from the following formula for Maximum Allowable Water Loading (MAWL):

$$\text{MAWL} = \frac{(0.9)\ (\text{Vessel Volume})}{(\text{Volume Multiplier at Max. Temp.})}$$

Loading Limits (MAWL)

LIQUID VOLUMES AND VAPOR PRESSURES FOR WATER IN A CLOSED VESSEL AT ELEVATED TEMPERATURES

Temperature °F	Temperature °C	Specific Volume of the Liquid, cu.ft./lb.	Vapor Pressure, psig	Volume Multiplier, $Sp.V_T/Sp.V_{77°F}$	% Volume Increase
77	25	.01607	—	1.00	0
212	100	.01672	0	1.04	4
392	200	.01853	211	1.15	15
482	250	.0201	562	1.25	25
540	282	.0215	948	1.34	34
572	300	.0225	1230	1.40	40
610	321	.0241	1650	1.50	50
660	349	.0278	2350	1.73	73
685	363	.0315	2780	1.96	96
700	371	.0369	3070	2.30	130
702	372	.0385	3120	2.40	140
704	373	.0410	3160	2.55	155
705	374	.0503	3190	3.13	213
(Critical Point)					

Data from Keenan & Keyes, "Thermodynamic Properties of Steam," John Wiley & Sons, Inc., New York

Loading Limits (MAWL)

Example:

What is the maximum volume of a water slurry which can be treated safely to 300 °C in a 1000 mL vessel? Substituting in the above formula:

$$MAWL = \frac{(0.9)\ (1000)}{1.4} = 643 \text{ mL}$$

From the above it is clear that the vessel should not be charged with more than 643mL of slurry at room temperature.

Advice

- Make sure there is a safety factor on the rupture disc and vessel which is greater than any potential temperature overshoot.
- Use a PID controller where a set temperature limit can be inputted. Prevents people from accidently setting a temperature that is too high.
- Place thermocouple feeding PID controller close to vessel wall.
- Have vessels professionally pressure tested.
- Leak test vessels by leaving overnight with a few bars of compressed air.
- Reassess if a new solvent is used, calculations will change.

Question and answer session

- Thank you for listening,
- Any Questions?