

## Selected slides from **CL152: Intro to Chem Engg**

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Set: 4

### **Procedure for Energy Balance Calculations**

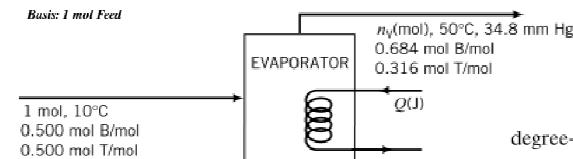
1. Make material balance calculations to find flow rates (or masses) of all streams.
2. Write the generalized energy balance equation and cancel all the terms that are either zeros or can be neglected.
3. Choose reference states for each species involved (T P state composition). A proper choice of the reference states enables easy calculation of enthalpies and energy balances.
4. Construct an inlet-outlet enthalpy table with mass or molar flow rates for open systems and initial-final amounts of species and internal energies for closed systems.
5. Estimate the specific enthalpies or internal energies and insert in the Table constructed in step 4. e.g., construct process paths to determine specific enthalpies.
6. Solve the simplified energy balance equation in step 2 for the unknown.

## Example 8.4-4 Example of Simultaneous energy + material balance with use of process enthalpy table to solve

### *Partial Vaporization of a Mixture*

An equimolar liquid mixture of benzene (B) and toluene (T) at 10°C is fed continuously to a vessel in which the mixture is heated to 50°C. The liquid product is 40.0 mole % B, and the vapor product is 68.4 mole % B. How much heat must be transferred to the mixture per g-mole of feed?

Basis: 1 mol Feed



degree-of-freedom analysis:

$n_V(mol), 50^\circ\text{C}, 34.8$   
0.684 mol B/mol  
0.316 mol T/mol

3 unknown variables ( $n_V, n_L, Q$ )  
-2 material balances  
-1 energy balance  
= 0 degrees of freedom

**Total Mass Balance:**

**Benzene Balance:**

$$\begin{aligned} 1.00 \text{ mol} &= n_V + n_L \\ 0.500 \text{ mol} &= 0.684n_V + 0.400n_L \end{aligned} \quad \Rightarrow \quad \begin{aligned} n_V &= 0.352 \text{ mol} \\ n_L &= 0.648 \text{ mol} \end{aligned}$$

## Example 8.4-4 Example of Simultaneous energy + material balance

References: B(l, 10°C, 1 atm), T(l, 10°C, 1 atm)

### Use enthalpy table

Substance Species	IN			OUT		
	Stream - 1 (liq) 10°C	Stream - 2 (liq) 50°C	Stream - 3 (vap) 50°C	n <sub>in</sub>	n <sub>out</sub>	n <sub>vap</sub>
1 B(l)	0.500	0	0	0.259	1.381	0
2 T(l)	0.500	0	0	0.389	2.47	0
3 B(v)	0	-	0	0	0.241	9.04
4 T(V)	0	-	0	0	0.111	4.77
H <sub>in</sub>	$(\sum n_i H_i)_1 = 0$		$(\sum n_i H_i)_2 = 3.85$	$(\sum n_i H_i)_3 = 13.81$		
H <sub>in/out</sub>	$(\sum n_i H_i)_m = 0$		$(\sum n_i H_i)_{out} = 17.66$			

### Example 8.4-4 Example of Simultaneous energy + material balance

Given Data / looked-up Data

$$C_p B(e) = 126.5 + 23.4T \quad \text{where } T \text{ is in } {}^\circ\text{C}$$

$$C_p T(e) = 148.8 + 32.4T$$

$$C_p B(v) = 74.06 + 32.95T - 25.2T^2 + 77.57T^3$$

$$C_p T(v) = 94.18 + 38T - 27.86T^2 + 80.33T^3$$

$$\hat{\Delta H}_v B = 30.765 \text{ kJ/mole} \quad \text{at } 80.1 {}^\circ\text{C}$$

$$\hat{\Delta H}_v L = 33.47 \text{ kJ/mole} \quad \text{at } 110.62 {}^\circ\text{C}$$

### Example 8.4-4 Example of Simultaneous energy + material balance

$$\hat{H}_1 = \int_{10 {}^\circ\text{C}}^{50 {}^\circ\text{C}} C_p B(e) dT = 5.332 \text{ kJ/mole}$$

$$\hat{H}_2 = \int_{10 {}^\circ\text{C}}^{50 {}^\circ\text{C}} C_p T(e) dT = 6.340 \text{ kJ/mole}$$

$$\begin{aligned} \hat{H}_3 &= \int_{10}^{80.1} C_p B(e) dT \\ &\quad + \hat{\Delta H}_v B \Big|_{80.1 {}^\circ\text{C}} \end{aligned}$$

$$+ \int_{80.1 {}^\circ\text{C}}^{50 {}^\circ\text{C}} C_p B(v) dT = 37.52 \text{ kJ/mole}$$

$$\begin{aligned} \hat{H}_4 &= \int_{10}^{110.62} C_p T(e) dT + \hat{\Delta H}_v T \Big|_{110.62 {}^\circ\text{C}} + \int_{110.62 {}^\circ\text{C}}^{50 {}^\circ\text{C}} C_p T(v) dT = \\ &\quad 42.93 \text{ kJ} \end{aligned}$$

**Example of Simultaneous energy + material balance  
with use of process enthalpy table to solve**

Example 8.4-4

$$\text{Energy balance : } \Delta H + \cancel{\Delta E_p} + \cancel{\Delta E_k} = Q - \cancel{W_s}$$

$$\Delta H = Q$$

$$\Delta H = \sum n \hat{H}_{\text{out}} - \sum n \hat{H}_{\text{in}}$$

$$= 17.66 - 0 = Q$$

$$\Rightarrow Q = 17.66 \quad \boxed{\text{kJ/mole feed}}$$

### Energy + material balance with chemical reaction

1. This is the most general class of problems where chemical reactions are also involved.
2. Example: Reactors of various sorts ...
3. Basic quantity: the heat of reaction  $\Delta \hat{H}_r(T, P)$

It is the enthalpy change for a process in which stoichiometric quantities of reactants at temperature T and pressure P react completely in a single reaction to form products at the same temperature and pressure.

## Measuring $\hat{\Delta}H_r(T, P)$

1. The heat of reaction may be measured in closed reactor immersed in a fluid contained in a well-insulated vessel (called calorimeter).
2. The system is kept at T, P and reaction conducted
3. The rise or fall of the fluid temperature can be measured and used to determine the energy released or absorbed by the reaction, and related to  $\hat{\Delta}H_r(T, P)$

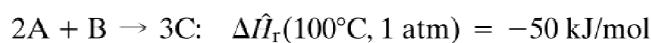
## Enthalpy change in chemical reactions

1. Heat of reaction specified at T, P, state
2. The standard heat of reaction:  $\overset{\wedge}{\Delta}H_r^{\circ}$  or  $\hat{\Delta}H_r(T_0, P_0)$ 

It is the difference between total enthalpy of products and total enthalpy of reactants at  $T_0=25^\circ\text{C}$  and  $P_0=1 \text{ atm}$  when stoichiometric quantities of reactants react to produce products.  
The units of  $\overset{\wedge}{\Delta}H_r^{\circ}$  are usually kJ/mol.

## Enthalpy change in chemical reactions

3. Important note: The units of  $\Delta\hat{H}_r(T, P)$  are kJ/mol, but be careful of what per mol means: in the chemical reaction:



it means:

$$\frac{-50 \text{ kJ}}{2 \text{ mol A consumed}} = \frac{-50 \text{ kJ}}{1 \text{ mol B consumed}} = \frac{-50 \text{ kJ}}{3 \text{ mol C generated}}$$

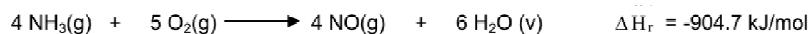
so for 150 mol C generated,

$$\Delta\dot{H} = \frac{-50 \text{ kJ}}{3 \text{ mol C generated}} \mid \frac{150 \text{ mol C generated}}{\text{s}} = -2500 \text{ kJ/s}$$

## Enthalpy change in chemical reactions

3. Another example of what /mol means:

e.g.:



This means that if 4 moles of  $\text{NH}_3(\text{g})$  react with 5 moles of  $\text{O}_2(\text{g})$  to make 4  $\text{NO}(\text{g})$  and 6  $\text{H}_2\text{O}(\text{v})$  at  $25^\circ \text{C}$ , the difference between total enthalpy of products and total enthalpy of reactants is 904.7 kJ/mol.

4. In the above, enthalpy change per mole of  $\text{O}_2$  is  $-904.7/5$ , and similar for others  
 5. The numbers -4,-5,4,6 above are the stoichiometric coefficients,  $v_i$

## Enthalpy change in chemical reactions

6. Choose as references molecular species at T and P where heat of reaction is specified. Standard heat of reaction is estimated at 25°C and 1 atm; so, usually we choose this as the reference. P has negligible effect of heat of reaction. The phases of the species should be same as the phase in the reaction at 25°C

## Enthalpy change in chemical reactions

7. Remember extent of reaction:

$$\xi = \frac{|n_{A,out} - n_{A,in}|}{|\nu_A|} = \frac{n_{A,r}}{|\nu_A|}$$

8. So the enthalpy of a reaction with extent  $\xi$  is (at  $T_0=25^\circ\text{C}$  and  $P_0=1\text{ atm}$  ):

$$\Delta H = \xi \hat{\Delta H}_r(T_0, P_0)$$

## Energy + material balance with chemical reaction

9. Basic balance with chemical rection(s): involves heat of those reactions

$$\dot{\Delta H} = \dot{\xi} \Delta H_r^{\circ} + \sum \dot{n}_{out} \dot{H}_{out} - \sum \dot{n}_{in} \dot{H}_{in} \quad \text{Single rxn}$$

## Energy + material balance with chemical reaction

9. Basic balance with chemical rection(s): involves heat of those reactions

$$\dot{\Delta H} = \dot{\xi} \Delta H_r^{\circ} + \sum \dot{n}_{out} \dot{H}_{out} - \sum \dot{n}_{in} \dot{H}_{in} \quad \text{Single rxn}$$

$$\dot{\Delta H} = \sum \dot{\xi} \Delta H_r^{\circ} + \sum \dot{n}_{out} \dot{H}_{out} - \sum \dot{n}_{in} \dot{H}_{in} \quad \text{Multiple rxn}$$

## Enthalpy change in chemical reactions

10. At other temperatures and pressures,  
use the state-independence concept and  
a suitable hypothetical path

## Enthalpy change in chemical reactions

Example: In ammonia oxidation, suppose ammonia and oxygen enter the reactor at 50C, 1 atm and the products emerge at 300C, 1 atm. The heat of reaction is available at 25C (called standard heat of reaction)

To solve, bring reactants from 50C to 25C, react them at 25C to generate products and then heat up the products to 300C. We follow this path because standard heat of reaction is available at 25C.

This method is called **Heat of Reaction** method.

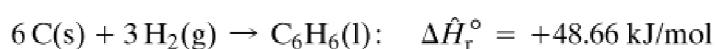
## Enthalpy change in chemical reactions

### Heat of Reaction method:

1. Bring reactants from inlet conditions to 25C, 1atm.
2. react them at 25C to make products at 25C and
3. then take the products to outlet conditions.
4. Add the enthalpy changes in the three above steps.

## Heat of Formation

- The formation reaction of a compound is the reaction in which the compound is formed from its elemental constituents as they normally occur in nature (e.g., O<sub>2</sub> not O).
- The enthalpy change associated with the formation of 1 mole of the compound at a reference temperature and pressure (usually 25 C and 1 atm) is the heat of formation of the compound. E.g. for benzene:



## Enthalpy change in chemical reactions

Alternative to Heat of Reaction method:

### Heat of Formation method:

Choose as references elemental species that make up the reactants and products at 25C and 1 atm in the phase in which they appear in the heat of formation.

Enthalpy of each molecular species is found by the following process path:

Make the molecular species from the elemental species at 25C and subject the molecular species to isobaric and isothermal conditions to take it to the inlet/outlet conditions.

$$\dot{\Delta H} = \sum \dot{n}_{\text{out}} \dot{H}_{\text{out}} - \sum \dot{n}_{\text{in}} \dot{H}_{\text{in}}$$

## Enthalpy change in chemical reactions

Alternative to Heat of Reaction method:

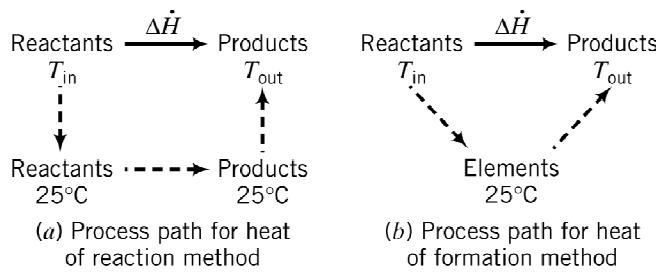
### Heat of Formation method:

1. Bring reactants from inlet conditions to their constituent elements at 25C,
2. Take the elements at 25C to outlet
3. Add the enthalpy changes in the two above steps. We are automatically accounting for the heat of reaction term.

$$\dot{\Delta H} = \sum \dot{n}_{\text{out}} \dot{H}_{\text{out}} - \sum \dot{n}_{\text{in}} \dot{H}_{\text{in}}$$

## Enthalpy change in chemical reactions

Heat of Reaction method vs. Heat of Formation method:



## Enthalpy change in chemical reactions

Back to Heat of Reaction method:

For the Heat of Reaction method, we need  $\Delta\dot{H}_r^\circ$

How to get  $\Delta\dot{H}_r^\circ$ ?

1. Directly determine heat of reaction experimentally
2. Use standard heat of reaction  $\Delta\dot{H}_r^\circ$
3. Use heat of formations to get  $\Delta\dot{H}_r^\circ$

Use Heat of formations to get  $\Delta H_r^\circ$  :

$$\Delta H_r^\circ = \sum \left( v \Delta H_f^\circ \right)_{\text{products}} - \sum \left( v \Delta H_f^\circ \right)_{\text{reactants}}$$

$\Delta H_f^\circ$  is standard heat of formation

## Enthalpy change in chemical reactions

If none of the above are possible, try:

Hesse's Law. It uses related reactions to  
get a desired heat of reaction  $\Delta H_r^\circ$

## Hess's Law to get $\Delta H$

- Hess's Law: If the stoichiometric equation for reaction 1 can be obtained by algebraic operations (multiplication by constants, addition, and subtraction) on stoichiometric equations for reactions 2, 3, . . . , then the heat of reaction can be obtained by performing the same operations on the heats of reactions of reactions 2, 3, . . . .

## Example of Hess's Law to get $\Delta H$

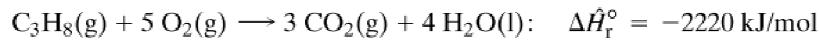
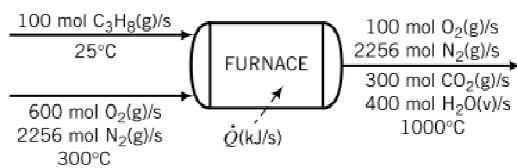
- Given standard heats of reactions:
  1.  $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O: \Delta\hat{H}_{r1}^\circ = -1559.8 \text{ kJ/mol}$
  2.  $C + O_2 \rightarrow CO_2: \Delta\hat{H}_{r2}^\circ = -393.5 \text{ kJ/mol}$
  3.  $H_2 + \frac{1}{2}O_2 \rightarrow H_2O: \Delta\hat{H}_{r3}^\circ = -285.8 \text{ kJ/mol}$
- Calculate heat of reaction for:
  4.  $2C + 3H_2 \rightarrow C_2H_6: \Delta\hat{H}_{r4}^\circ = ?$

## Example of Hess's Law to get $\Delta H$

- Given standard heats of reactions:
  - $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2 CO_2 + 3 H_2O: \Delta\hat{H}_{r1}^\circ = -1559.8 \text{ kJ/mol}$
  - $C + O_2 \rightarrow CO_2: \Delta\hat{H}_{r2}^\circ = -393.5 \text{ kJ/mol}$
  - $H_2 + \frac{1}{2}O_2 \rightarrow H_2O: \Delta\hat{H}_{r3}^\circ = -285.8 \text{ kJ/mol}$
- Calculate heat of reaction for:
  - $2 C + 3 H_2 \rightarrow C_2H_6: \Delta H_{r4}^\circ = ?$
- Solution: Note  
 $(4) = 2 \times (2) + 3 \times (3) - (1)$
- So:  $\Delta\hat{H}_{r4}^\circ = 2\Delta\hat{H}_{r2}^\circ + 3\Delta\hat{H}_{r3}^\circ - \Delta\hat{H}_{r1}^\circ = -84.6 \text{ kJ/mol}$

## Typical situation/problem statement

- Calculate Q for:



## Procedure for Energy Balance with Rxn

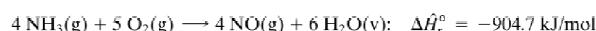
1. Make material balance calculations of all streams.
2. Choose reference states for each species involved (T P state composition). (a) for Heat of Rxn method, reactants at 25C 1atm or inlet stream state; (b) for Heat of Formation method, elements at 25C 1 atm and for non-reacting species at any constant temperature.
3. Calculate extent of reaction(s)  $\xi$  based on reactant(s) whose flow rates are known.
4. Prepare Inlet-Outlet enthalpy table
5. Estimate the specific enthalpies or internal energies and insert in the Table constructed in step 4. e.g., construct process paths to determine specific enthalpies.
6. Solve the simplified energy balance equation.

Example 9.5-1

## Example of Simultaneous energy + material balance with reaction

### *Energy Balance About an Ammonia Oxidizer*

The standard heat of reaction for the oxidation of ammonia is given below:

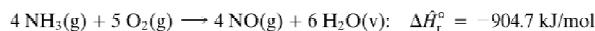


One hundred mol  $\text{NH}_3/\text{s}$  and 200 mol  $\text{O}_2/\text{s}$  at 25°C are fed into a reactor in which the ammonia is completely consumed. The product gas emerges at 300°C. Calculate the rate at which heat must be transferred to or from the reactor, assuming operation at approximately 1 atm.

## Example 9.5-1 Example of Simultaneous energy + material balance with reaction

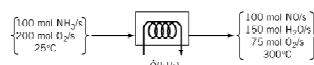
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*Basis: Given Feed Rates*



*References:  $\text{NH}_3(\text{g}), \text{O}_2(\text{g}), \text{NO}(\text{g}), \text{H}_2\text{O}(\text{v})$  at 25°C and 1 atm*

Substance	$\dot{n}_{\text{in}}$ (mol/s)	$\dot{H}_{\text{in}}$ (kJ/mol)	$\dot{n}_{\text{out}}$ (mol/s)	$\dot{H}_{\text{out}}$ (kJ/mol)
$\text{NH}_3$	100	0	—	—
$\text{O}_2$	200	0	75	$\dot{H}_1$
$\text{NO}$	—	—	100	$\dot{H}_2$
$\text{H}_2\text{O}$	—	—	150	$\dot{H}_3$

**Use  
better  
table!**

## Example 9.5-1 Example of Simultaneous energy + material balance with reaction

### *Energy Balance About an Ammonia Oxidizer*

#### *Calculate Unknown Enthalpies*

$\text{O}_2(\text{g}, 300^\circ\text{C})$ : From Table B.8,  $\dot{H}_1 = 8.470 \text{ kJ/mol}$  (Insert value in enthalpy table)

$\text{NO}(\text{g}, 300^\circ\text{C})$ :  $\dot{H}_2 = \int_{25^\circ\text{C}}^{300^\circ\text{C}} (C_p)_{\text{NO}} dT \xrightarrow{\text{Table B.2}} \dot{H}_2 = 8.453 \text{ kJ/mol}$  (Insert in table)

$\text{H}_2\text{O}(\text{v}, 300^\circ\text{C})$ : From Table B.8,  $\dot{H}_3 = 9.570 \text{ kJ/mol}$  (Insert in table)

#### *Calculate $\dot{\xi}$ and $\Delta\dot{H}$*

Since 100 mol  $\text{NH}_3/\text{s}$  is consumed in the process ( $A = \text{NH}_3$ ,  $\dot{n}_{A,r} = 100 \text{ mol NH}_3 \text{ consumed/s}$ ), Equation 9.1-3 becomes

$$\dot{\xi} = \frac{\dot{n}_{\text{NH}_3,r}}{|\nu_{\text{NH}_3}|} = \frac{100 \text{ mol/s}}{4} = 25 \text{ mol/s}$$

↓ Equation 9.5-1a

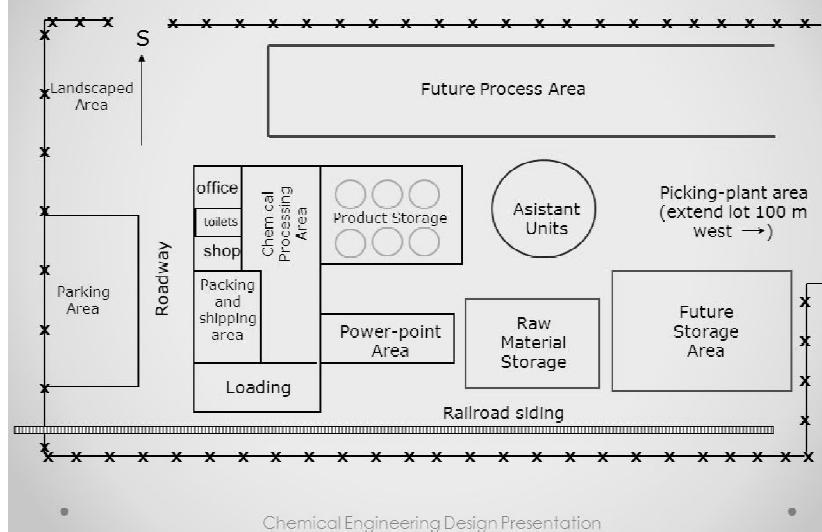
$$\Delta\dot{H} = \dot{\xi}\Delta\hat{H}_r^\circ + \underbrace{\sum \dot{n}_{\text{out}}\dot{H}_{\text{out}} - \sum \dot{n}_{\text{in}}\dot{H}_{\text{in}}}_{\text{from table}}$$

$$= (25 \text{ mol/s})(-904.7 \text{ kJ/mol}) + [(75)(8.470) + (100)(8.453) + (150)(9.570) - (100)(0) - (200)(0)] \text{ kJ/s} = -19,700 \text{ kJ/s}$$

## Layout of a chemical process plant



### Plant Layout

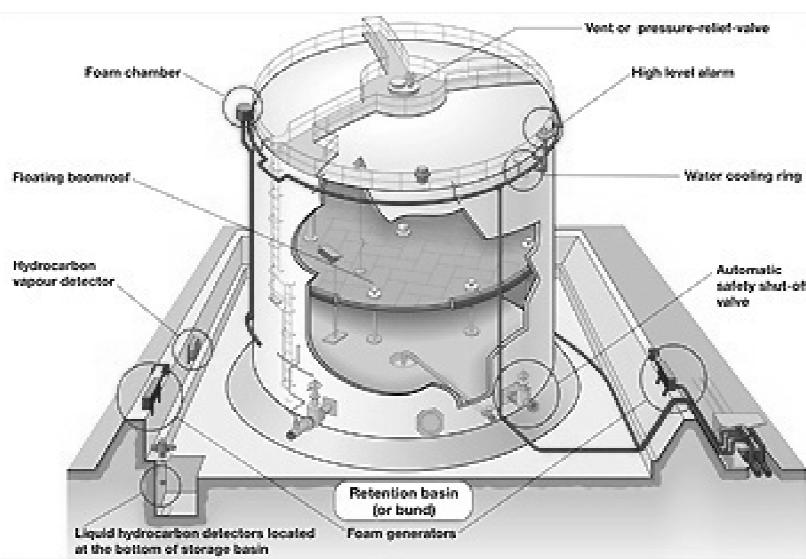


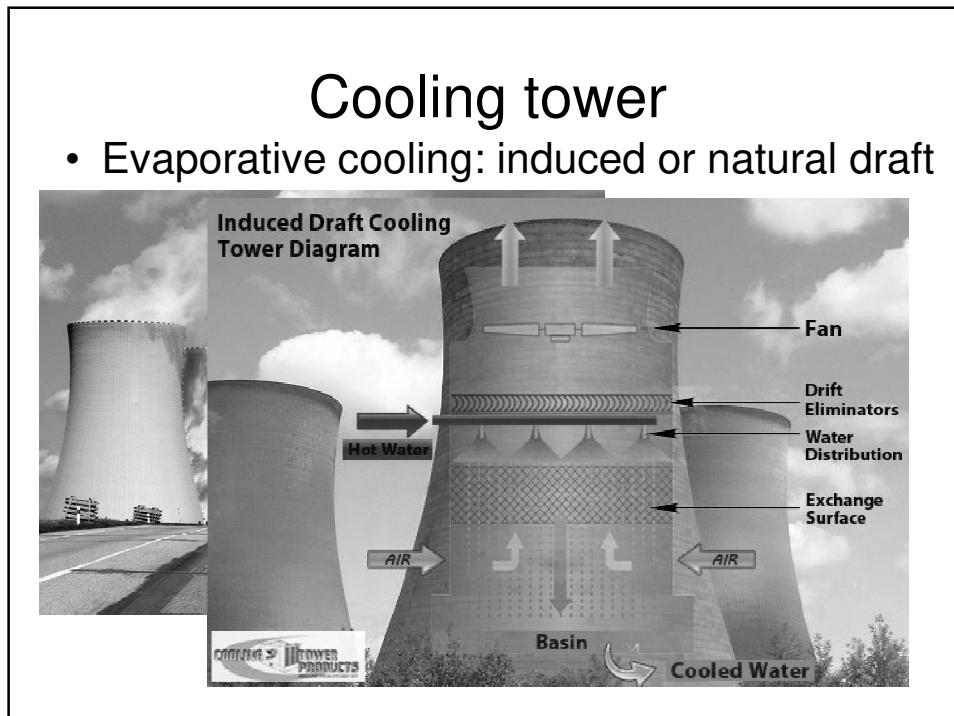
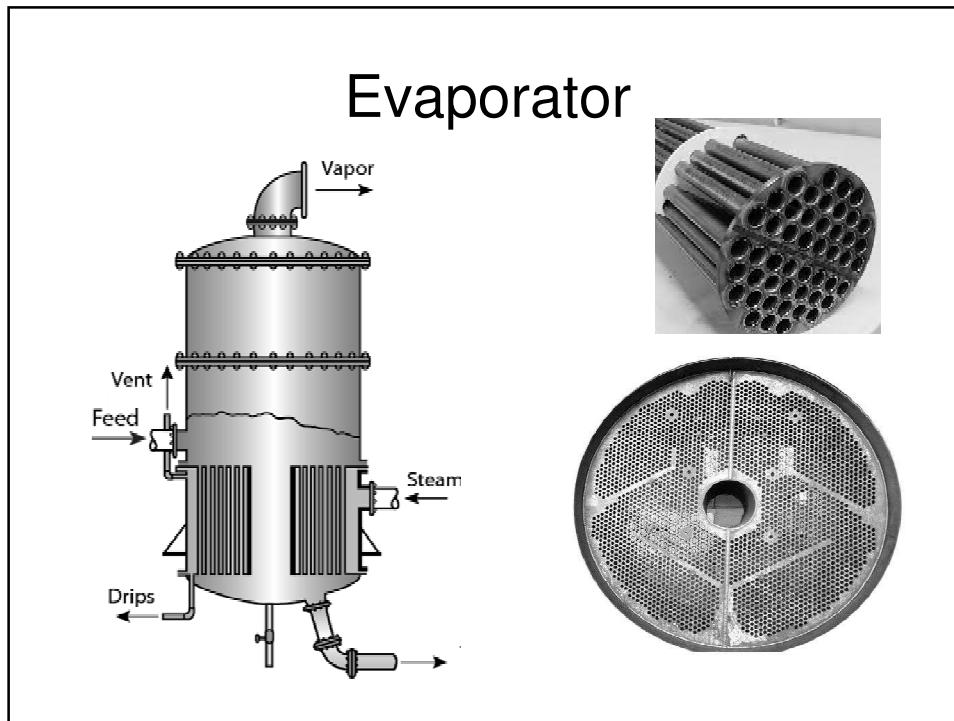
## Storage tanks for liquids

- Tank farm



## Storage tanks for liquids





## Storage tanks: Horton sphere

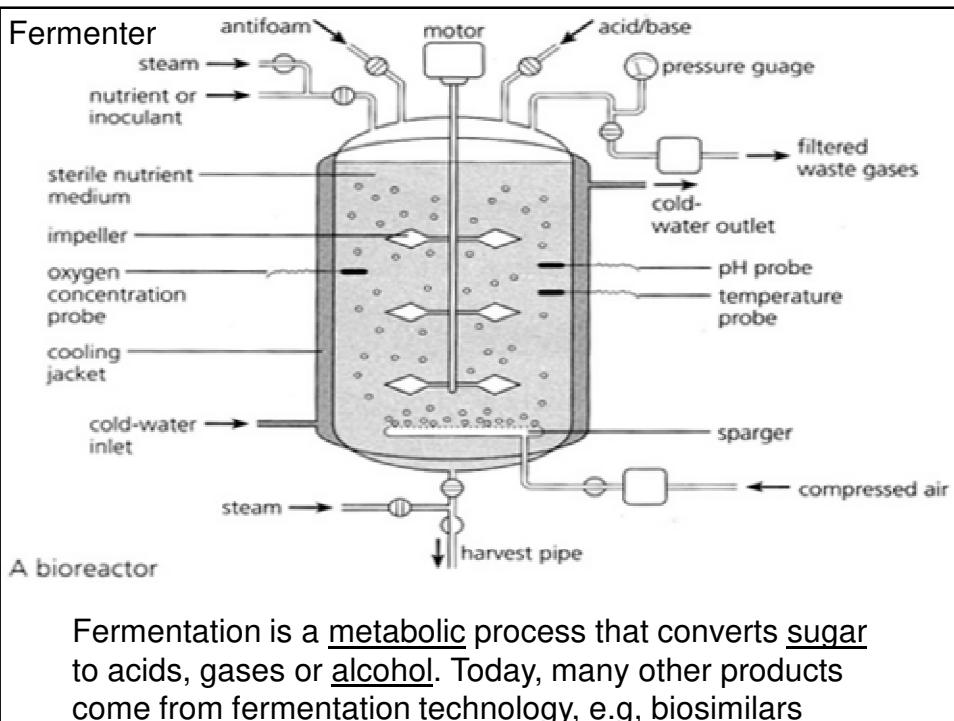
- The Horton sphere is a spherical pressure vessel, which is used for storage of compressed gases such as propane, Liquefied petroleum gas or butane in a liquid gas stage



## Solids storage



# Reactors



## **Safety: Fire at bio-diesel plant in Visakhapatnam SEZ 21 April 2016**



Engineers make things,  
including materials, for a  
specific need, in a safe and  
economical way.

End of my lectures ... Thanks!