ABE 201
Biological Thermodynamics 1

Module 6:

Mass Balances with

Chemical Reactions

Outline

- Conservation of Mass and Chemical Reactions

- Useful Concepts for Solving Mass Balances with Chemicals Reactions

- Approaches to Solving Mass Balances with Chemical Reaction

Conservation of Mass

Accumulation = In – Out + Generation - Consumption

- **Steady-state: Accumulation = 0**
- **No chemical Reactions: Gen = Con = 0**
- **Chemical Reactions?**
  - **Two Approaches**
  - **Atomic Species Balance**
  - **Chemical Compound Balance**

Concepts

- Stoichiometry: balanced chemical reaction that is mathematical representation of the relationship between atoms in reactants and atoms in products
- Yield: amount of actual product produced divided by theoretical product that could be produced

$$Yield = \frac{Actual\ Product}{Theoretical\ Product}$$

Stoichiometry

To start, lets consider the burning of ethanol in the presence of oxygen which produces carbon dioxide and water.

$$C_2H_5OH + O_2 \longrightarrow CO_2 + H_2O$$

As the equation is given, this is ***not*** a balanced stoichiometric equation.

Stoichiometry

To balance this equation, you must have equal amounts of each component on each side of the equation.

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

Carbon - 2	Carbon - 2
Hydrogen - 6	Hydrogen -6
Oxygen - 7	Oxygen - 7

Balancing a chemical reaction is really an ***atomic*** mass balance! (In -> Out)

Stoichiometry

- Describes the relationship between <u>moles</u> of reactants and products <u>if and when</u> a chemical reaction occurs
- Does <u>**not**</u> tell us
  - that the reaction <u>in fact</u> occurred in this system;
  - how <u>fast</u> it occurred;
  - how <u>completely</u> the reaction occurred

Stoichiometry vs Yield

2 mole C_2H_5OH

6 moles O_2

1 moles C_2H_5OH

3 moles O_2

3 moles H_2O

2 moles CO_2

$$1C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

$$Yield_{H_2O} = \frac{3}{6} = 0.50$$

Extent of Reaction (ξ)

A variable to describe generation and consumption

extent of reaction = $\xi \equiv (n_{i,out} - n_{i,in})/v_i$

$n_{i,in}$ = moles of compound i going in

$n_{i,out}$ = moles of compound i going out

v_i = stoichiometric coefficient for compound i

Note: v_i is negative for reactants
v_i is positive for products

$$1C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

$v_{ethanol} = -1$ $v_{CO2} = +2$

$v_{oxygen} = -3$ $v_{water} = +3$

Extent of Reaction and ICE Method

Initial	Change	Equilibrium
In	Extent	Out

Accumulation = In – Out + Generation - Consumption

$$\boldsymbol{0 \;=\; In \;-\; Out \;+\; v_i * \xi * MW_i}$$

Sign of v_i determines if it's
+ <u>generation (product)</u> or
- <u>consumption (reactant)</u>

Metabolism of Glucose

Glucose ($C_6H_{12}O_6$) is converted to water and carbon dioxide through <u>cellular respiration</u> in a bioreactor.

a) Write the balanced stoichiometric equation for respiration.

b) Glucose is fed into the bioreactor at a rate of 120 g/hr. Oxygen is fed at 150 g/hr. Which is the limiting reagent?

c) A gas chromatograph measures CO_2 leaving the bioreactor at 132 g/hr. What is the extent of reaction if the feed conditions from b) are used? Assume no CO_2 enters the reactor.

a) $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

b) 120 g/hr / 180 g/mol = 0.667 mol/hr glu

150 g/hr / 32 g/mol = 4.69 mol/hr glu

0.67 mol glu requires 0.67*6 =4 moles of O_2
So oxygen is in excess, glucose is <u>limiting</u>.

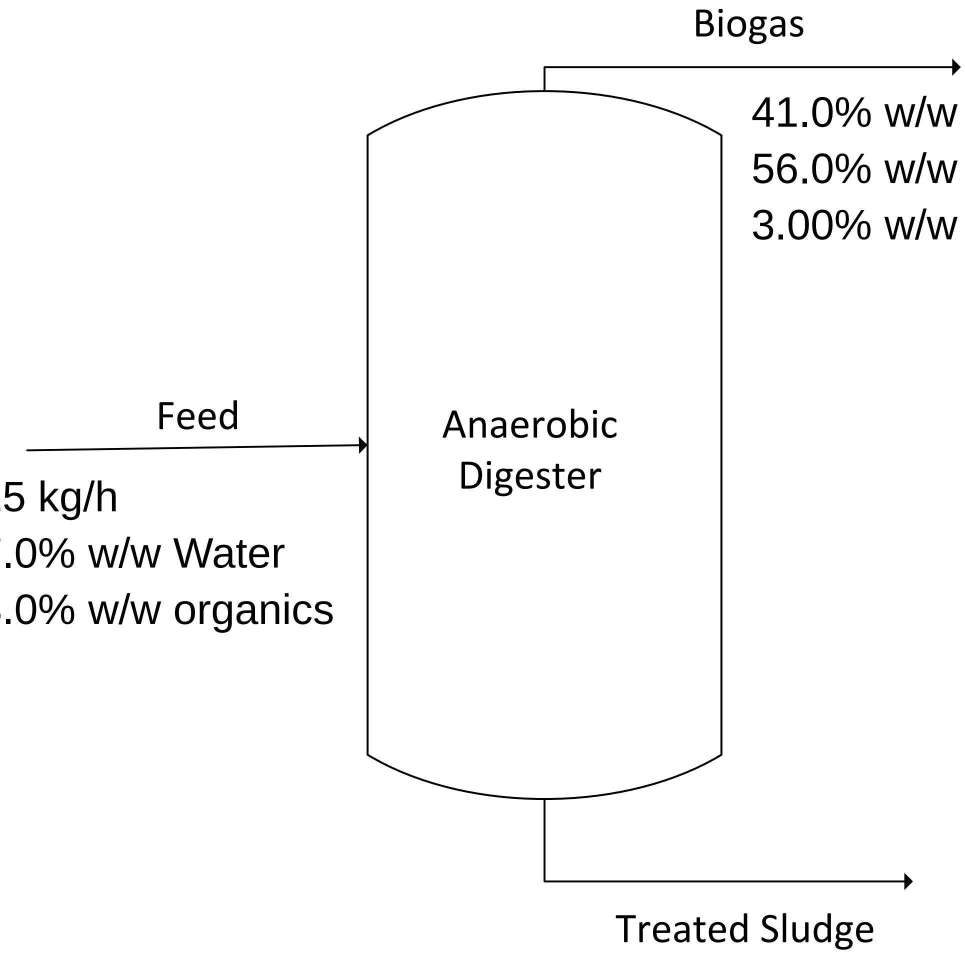
c) $\boldsymbol{0 = In - Out + v_i * \xi * MW_i}$

$0 = 0 - 132\text{ g/hr} + 6 * \xi * 44\text{ g/mol}$

$\xi = 0.50$ mol/hr

Anaerobic Digester

What is the rate of biogas production?



41.0% w/w Methane
56.0% w/w CO_2
3.00% w/w Hydrogen

225 kg/h
67.0% w/w Water
33.0% w/w organics

Organics
46.2% w/w C
12.8% w/w H
41.0% w/w O

87.0% w/w Water
13.0% w/w organics

	Feed	Biogas	Sludge
Water kg/h	150	0	?
BOD kg/h	75.0	0	?
CH4 kg/h	0	?	0
H2 kg/h	0	?	0
CO2 kg/h	0	?	0
total kg/h	225	?	?
x, Water	0.670	0	0.870
x, BOD	0.330	0	0.130
x, CH4	0	0.410	0
x, H2	0	0.030	0
x, CO2	0	0.560	0

$0 = In - Out$

$MW_{water} = 18$ kg/kmol
$MW_{Methane} = 16$ kg/kmol
$MW_{H2} = 2$ kg/kmol
$MW_{CO2} = 44$ kg/kmol

C

$0 = 75*0.462 -$
$(0.41*m2 *(1*12/16) + 0.56*m2*(1*12/44) + 0.13*m3*0.462)$

$0 = 34.65 - 0.460*m2 - 0.0601*m3$

H

$0 = 75*0.128+150*(2/18) -$
$(0.41*m2 *(4*1/16) + 0.03*m2*(1*2/2) + 0.13*m3*0.128+0.87*m3*(2*1/18))$

$0 = 26.27 - 0.1325*m2 - 0.1133*m3$

$$\begin{bmatrix} m_2 \\ m_3 \end{bmatrix} = \begin{bmatrix} 53.0 \\ 170 \end{bmatrix}$$

How to form mass balance equations for Atomic Species Balances

C

$$Mass_C = mass_{compound} \cdot \frac{moles_C}{moles_{Compound}} \cdot \frac{12\,{}^{g}\!/\!_{mol}}{g\ compound\,/\,mol}$$

25 g/min of xylose ($C_5H_{10}O_5$)

$$Mass_C = 25g/\min \cdot \frac{5}{1} \cdot \frac{12\,{}^{g}\!/\!_{mol}}{150g\ \text{xylose}\,/\,mol} \quad = 10g\ \text{C}/\min$$

$$Mass_H = 25g/\min \cdot \frac{10}{1} \cdot \frac{1\,{}^{g}\!/\!_{mol}}{150g\ \text{xylose}\,/\,mol} \quad = 1.7g\ \text{C}/\min$$

$$Mass_O = 25g/\min \cdot \frac{5}{1} \cdot \frac{16\,{}^{g}\!/\!_{mol}}{150g\ \text{xylose}\,/\,mol} \quad = 13.3g\ \text{C}/\min$$

Xylose Fermentation

Xylose ($C_5H_{10}O_5$) is anaerobically fermented to ethanol (C_2H_5OH) and carbon dioxide by a genetically modified yeast. If we feed xylose into a bioreactor at a rate of 200 g/hr and the xylose is consumed at a rate of 180 g/h, what is the rate that xylose, ethanol, and carbon dioxide are leaving the reactor?

Assume no ethanol or carbon dioxide are fed into the reactor.

$C_5H_{10}O_5$ -> 5/3 C_2H_5OH + 5/3 CO_2

$$\boldsymbol{Con = v_i * \xi * MW_i}$$

$$\boldsymbol{Con_{xyl} = v_{xyl} * \xi * MW_{xyl}}$$

$$\boldsymbol{-180 g/hr = -1 * \xi * 150\ g/mol}$$

$$\boldsymbol{\xi = 1.2\ mol/hr}$$

Xylose

$acc = m_{xyl,in} – m_{xyl,out} + v_{xyl} * \xi * MW_{xyl}$

$0 = 200$ g/hr $– m_{xyl} - 1 * 1.2$ mol/hr*150 g/mol

$m_{xyl,out} = 20$ g/hr

Ethanol

$acc = m_{etoh,in} – m_{etoh,out} + v_{etoh} * \xi * MW_{etoh}$

$0 = 0 – m_{etoh,out} + 5/3 * 1.2$ mol/hr*46 g/mol

$m_{etoh,out} = 92$ g/hr

Carbon Dioxide

$acc = m_{co2,in} – m_{co2,out} + v_{co2} * \xi * MW_{co2}$

$0 = 0 – m_{co2,out} + 5/3 * 1.2$ mol/hr*44 g/mol

$m_{co2,out} = 88$ g/hr

Polyhydroxybutyrate (PHB)

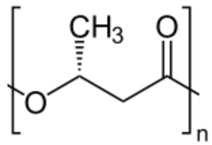
Glucose is converted to a bioplastic (PHB, $C_4H_6O_2$) using bacteria immobilized in a bioreactor at steady state. The bioreactor is fed a glucose syrup (50.0% water w/w) at 300. kg/h which is diluted by a recycle stream of water, residual (unreacted) glucose, and unrecovered PHB to become a solution that is 14.0% glucose (w/w) before entering the bioreactor.

Air (22.0% w/w oxygen, with N_2 and negligible CO_2) is sparged (bubbled) through the bioreactor at a rate of 227 kg/h to provide oxygen for the metabolism that make PHB. Unreacted oxygen, nitrogen gas, and carbon dioxide exit the reactor.

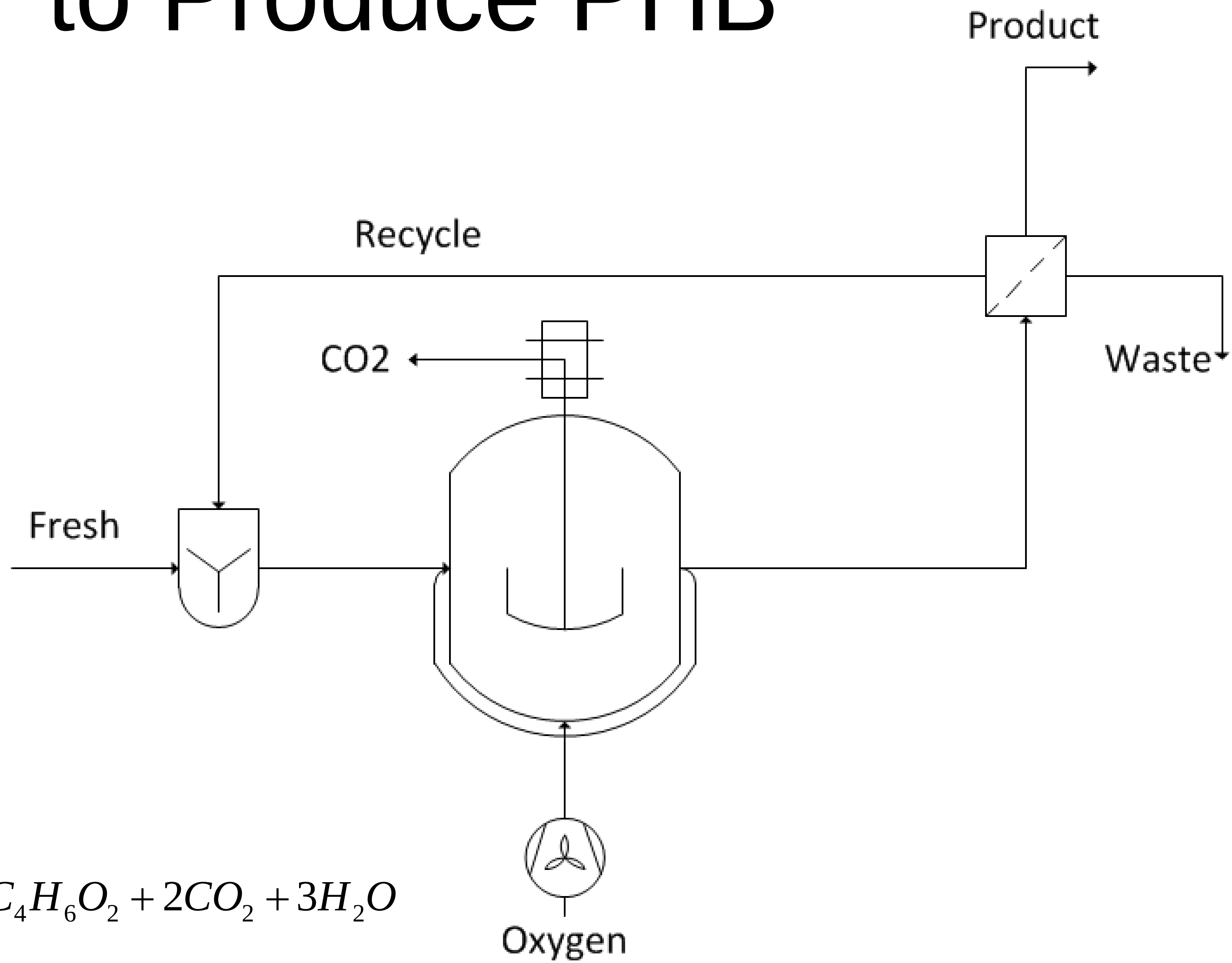
A waste stream (92.7% water, 7.30% glucose) is purged from the production system. The effluent from the reactor is filtered and recovered as a slurry that is 48.1% PHB, 48.1% water, and the rest residual glucose.

- What is the rate of production (kg/h) of product (PHB)?
- What is the yield of PHB from glucose?

Bioreactor With Recycle to Produce PHB



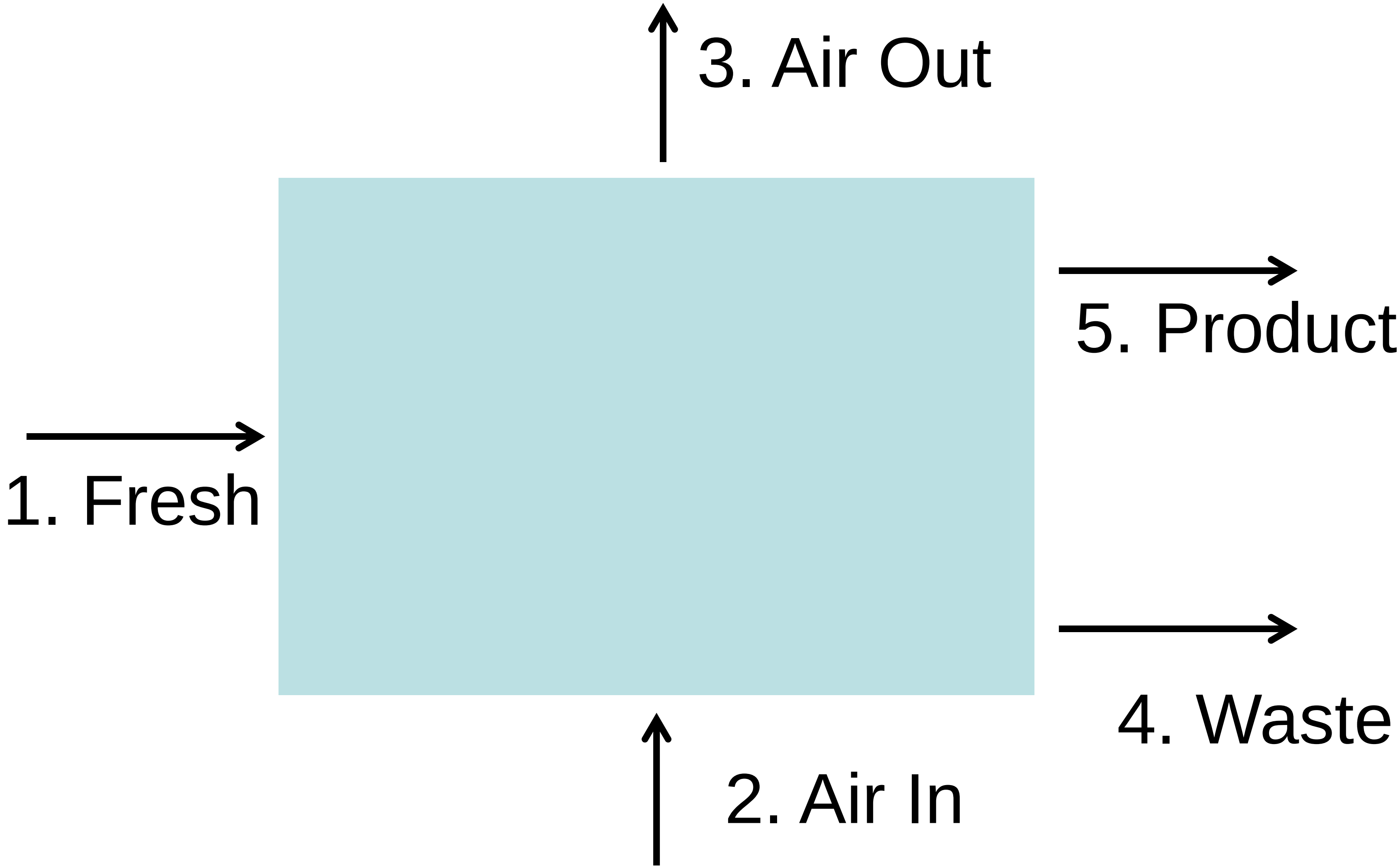
Polyhydroxybutyrate
(PHB)



$$C_6H_{12}O_6 + \frac{3}{2}O_2 \longrightarrow C_4H_6O_2 + 2CO_2 + 3H_2O$$

m kg/h	1. Fresh	2. Air In	3. Air Out	4. Waste	5. Product	6. Recycle
Total	300	227	?	?	?	?
Water	150	0	0	?	?	?
Glucose	150	0	0	?	?	?
PHB	0	0	0	?	?	?
Oxygen	0	49.9	?	0	0	0
CO2	0	0	?	0	0	0
N2	0	117	?	0	0	0

x kg/kg	1. Fresh	2. Air In	3. Air Out	4. Waste	5. Product	6. Recycle
x water	0.500	0	0	0.927	0.481	?
x glucose	0.500	0	0	0.073	0.038	?
x PHB	0	0	0	0	0.481	?
x Oxygen	0	0.220	?	0	0	0
x CO2	0	0	?	0	0	0
x N2	0	0.780	?	0	0	0



$$\text{DOF} = V - B - P - C$$
$$= 7 - 6 - 0 - 1 = 0$$

$$0 = In - Out + v_i * \xi * MW_i$$

MW_{water} = 18 g/mol = 18 kg/kmol
$MW_{glucose}$ = 180 g/mol = 180 kg/kmol
MW_{PHB} = 86 g/mol = 86 kg/kmol
MW_{O2} = 32 g/mol = 32 kg/kmol
MW_{CO2} = 44 g/mol = 44 kg/kmol
MW_{N2} = 28 g/mol = 28 kg/kmol

N2

$$0 = 177 - x_{3,N2} * m_{3,out}$$
$$0 = 177 - m_{N2,out}$$

$$m_3 = m_{N2,out} + m_{O2,out} + m_{CO2,out}$$

Water

$$0 = 150 - (0.481*m5 + 0.927*m4) + 3 * \xi * 18$$

Glucose

$$0 = 150 - (0.038*m5 + 0.073*m4) + -1 * \xi * 180$$

PHB

$$0 = 0 - (0.481*m5 + 0*m4) + 1 * \xi * 86$$

Oxygen

$$0 = (0.22*227) - m_{o2,out} + -1.5 * \xi * 32$$

CO2

$$0 = 0 - m_{co2,out} + 2 * \xi * 44$$

$$\begin{bmatrix} -150 \\ -150 \\ 0 \\ -49.9 \\ 0 \end{bmatrix} = \begin{bmatrix} -0.481 & -0.927 & 54 & 0 & 0 \\ -0.038 & -0.073 & -180 & 0 & 0 \\ -0.481 & 0 & 86 & 0 & 0 \\ 0 & 0 & -48 & -1 & 0 \\ 0 & 0 & 88 & 0 & -1 \end{bmatrix} \bullet \begin{bmatrix} m_4 \\ m_5 \\ \xi \\ m_{O2,out} \\ m_{CO2,out} \end{bmatrix}$$

$$\begin{bmatrix} m_4 \\ m_5 \\ \xi \\ m_{O2,out} \\ m_{CO2,out} \end{bmatrix} = \begin{bmatrix} 134 \\ 136 \\ 0.75 \\ 13.9 \\ 66.0 \end{bmatrix}$$

$$m_3 = m_{N2,out} + m_{O2,out} + m_{CO2,out}$$

$$= 177 + 13.9 + 66.0$$

$$= 256.9$$

$$m_{PHB} = x_{5,PHB} * m_5 = 0.481 * 134 = 64.5\ kg/h$$

$$yield_{PHB} = \frac{64.5\ kg/h / 86 kg/kmol}{150 kg/hr / 180 * 1/1} = 0.90$$

Summary

- Mass balances with chemical reactions can be solved in two ways:
  - Extent of reaction
  - Atomic species (elemental) balance
- Extent of Reaction
  - One number for each reaction, common to all reactants and products

$$\xi = (n_{i,out} - n_{i,in})/v_i$$

- Atomic species balances: gen=con=0