



IIT ROORKEE



NPTEL ONLINE
CERTIFICATION COURSE

WASTE TO ENERGY CONVERSION

ENERGY PRODUCTION FROM ORGANIC WASTES THROUGH FERMENTATION-2

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CHEMICAL ENGINEERING

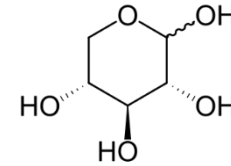
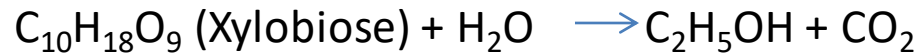
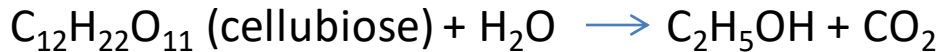
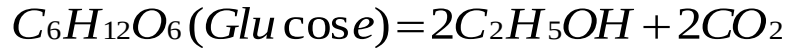


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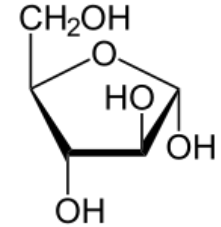
- Fermentation and energy production
- Production of ethanol from three different feedstocks and pre processing steps
- Production of ethanol from starchy crops (corn)
- Production of ethanol from lingo cellulosic biomass (LCB)
 - Pre treatment of lingo cellulosic biomass
 - Detoxification and hydrolysis
 - Fermentation, microorganisms and product recovery
- Ethanol production through gasification route
- Butanol production from LCB



Fermentation



Xylose



Arabinose

Ethanol yield

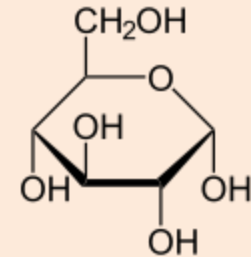
$$Y_{EtOH} = \frac{CV}{m}$$

Where, Y_{EtOH} is ethanol yield (g/kg),

C is ethanol concentration (g/L),

V is initial volume of liquid medium (L),

and m is the mass of the substrate (kg).



Glucose

Ethanol productivity

Amount of ethanol produced per unit of substrate utilized per unit of time. It is typically determined when ethanol concentration is maximal.

$$Q_{EtOH} = \frac{CV}{mt} = \frac{1000Y_{EtOH}}{t}$$

Where, Q_{EtOH} is the ethanol productivity (mg/kg h), and t is the time at which the ethanol concentration produced on substrates is maximum (h).

The maximum theoretical ethanol yield :

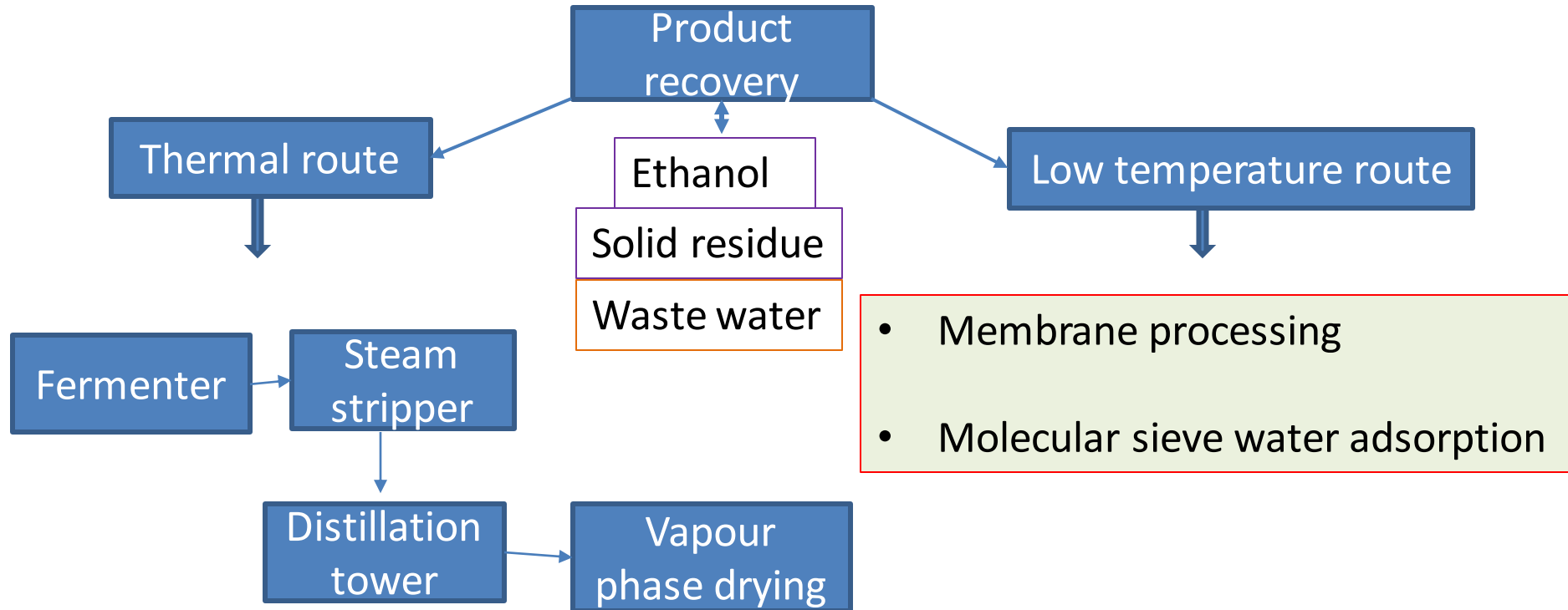
$$Y_{\max}(\%) = \frac{\text{Ethanol produced in reactor (g)}}{\text{Initial sugar in reactor (g)} \times 0.511} \times 100$$

Microorganisms for fermentation of LCB

- Sugar for starch based ethanol production is mostly hexose sugar (glucose), however, for LCBs mixer of pentose and hexose sugars are available.
- The most common and traditional microorganism for fermenting sugars into ethanol is a yeast, *Saccharomyces cerevisiae*, However, the natural strains of this yeast can ferment only six carbon sugars and hardly pentoses.
- Some yeast strains such as *Pichia stipitis*, *Candida shehatae*, and *Candida parapsilosis* can ferment xylose but not efficient for hexose fermentation
- Bacterial strains used for ethanol fermentation are *Zymomonas mobilis*, *Escherichia coli* and *Klebsiella oxytoca*, which have attracted a particular interest due to their capability to ferment hexose sugars rapidly
- Genetic modification of bacteria and yeast has produced strains capable of co-fermenting both pentoses and hexoses

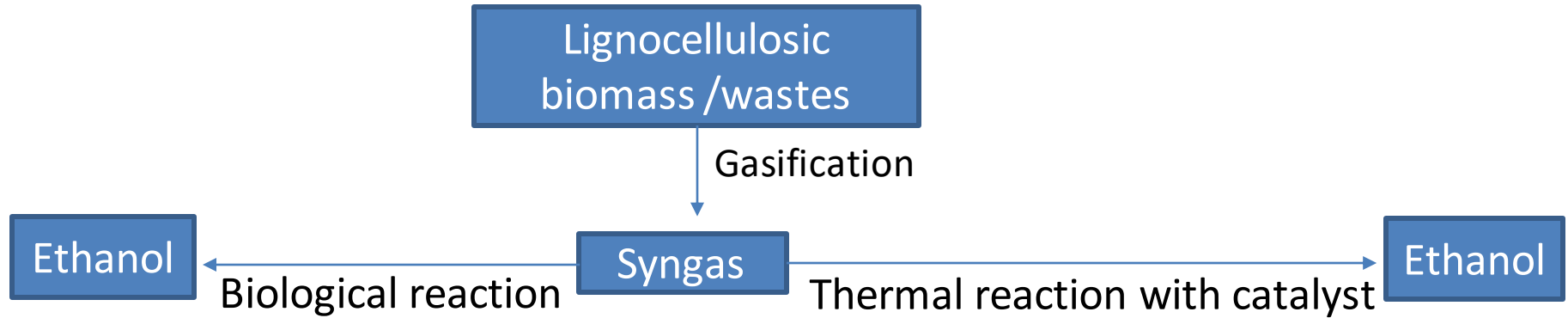


Product recovery



- The first process that was used in many of the earlier ethanol plants is the so-called azeotropic distillation or ternary distillation process (as opposed to a binary or two component distillation process). It consists of introducing a third component, benzene or cyclohexane, to the azeotropic solution which forms a heterogeneous azeotropic mixture. When this mixture is distilled, anhydrous ethanol is produced at the bottom of the distillation column.
 - ✓ (B.P. of ethanol 78.4 °C, water 100 °C, mixture 78.1 °C (95.5 % ethanol))
 - ✓ (B.P. of cyclohexane 80.7 °C, water 100 °C, mixture 69.8 °C (80 % cyclohexane))
- Another early method is called extractive distillation, which consists of adding a ternary component that increases the relative volatility of ethanol. In this case, anhydrous alcohol is produced and withdrawn at the top of the distillation column.
 - ✓ ethylene-glycol
- Some other methods: Salt distillation; Pressure swing distillation; Pervaporation

Alternate routes for ethanol production from lignocellulosic biomass/wastes



- Biological route uses *Clostridium ljungdahlii* bacteria.
- This microorganism ingest carbon monoxide, carbon dioxide and hydrogen and produce ethanol and water.

- Butanol is a major co-product of ABE (acetone, butanol and ethanol) fermentation as the typical proportions of acetone, butanol and ethanol are 3:6:1..
- *Clostridium* spp., particularly *C. acetobutylicum* or *C. beijerinckii* are capable of converting broad-ranging carbon sources (e.g. glucose, galactose, cellobiose, mannose, xylose and arabinose) to fuels and chemicals
- The ABE fermentation is biphasic involving acidogenesis and solventogenesis.
- Acidogenic phase involves the production of acids (e.g. acetic and butyric acid),
- Solventogenic phase is related to the production of solvents (e.g. acetone, butanol and ethanol).
- The ABE-producing bacteria can utilize both starchy and lignocellulosic substrates

- The butanol-producing clostridia can metabolize both pentose and hexose sugars in the biomass hydrolysates.
- Butanol toxicity to the fermenting microorganisms is a major barrier for the commercial bio production of the alcohol that limits its concentration in the fermentation broth.
- Butanol-producing bacterial cultures can rarely tolerate more than 2% butanol.
- Application of molecular techniques to the solventogenic clostridia has resulted in the development of hyper-butanol-producing strains such as *C. beijerinckii* P260 and *C. beijerinckii* BA101.
- Process for product recovery is also different with respect to ethanol

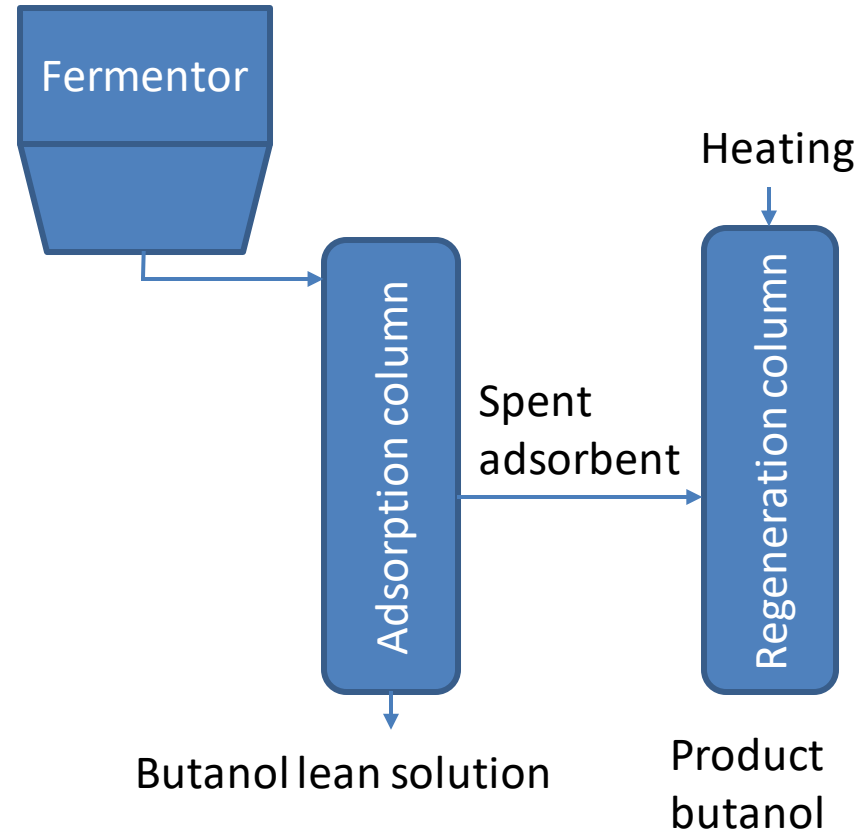
Butanol recovery

- The partial solubility of butanol in water creates impediments in its downstream processing and extraction from the fermentation broth.
- The high energy requirements subsequently add to the process expenditures making the overall butanol production expensive.
- To make ABE fermentation profitable, many *in situ* product recovery systems have been developed; a few of which include adsorption, liquid-liquid extraction, pervaporation, gas stripping and supercritical fluid extraction.
- The research on these butanol recovery techniques is still at infancy stage, and none of these technologies have been implemented at the commercial level.



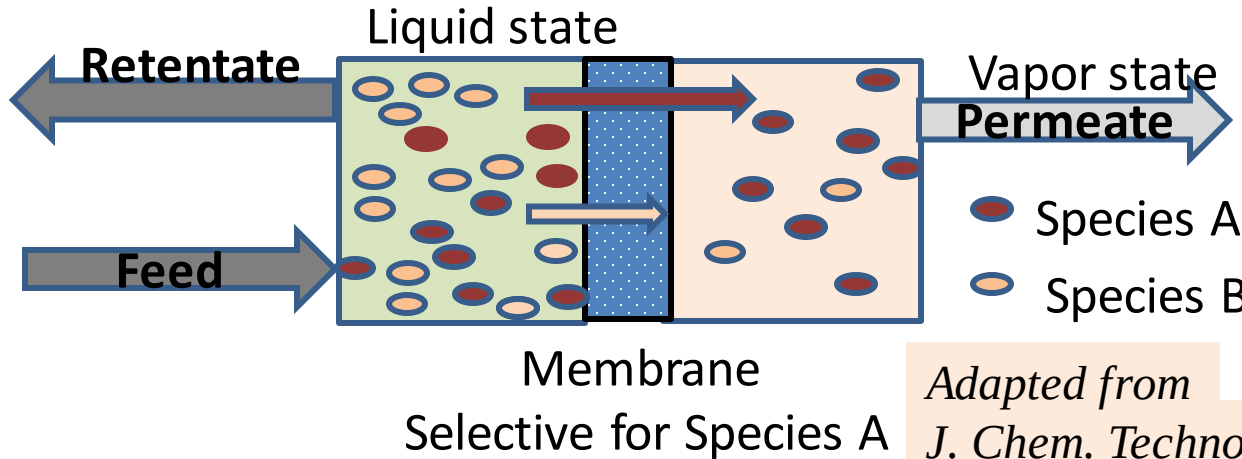
Representation of butanol recovery by adsorption

- Adsorption of butanol onto a packed column from the dilute solution or fermentation broth followed by desorption by heat treatment or displacer
- Activated carbon, zeolite and polymeric resins, silicalite (790–810 g/L), adsorbent resins, amberlite, polyvinyl pyridine, are thoroughly studied for butanol recovery



Representation of butanol recovery by pervaporation

- It is a membrane-based recovery technique that employs a non-porous or molecularly porous membrane. One side of the membrane is brought into contact with the fermentation broth while on the other side vacuum or gas purge is applied to create permeate vapor stream. The components from the feed liquid diffuse through the membrane and evaporate into the permeate vapor phase

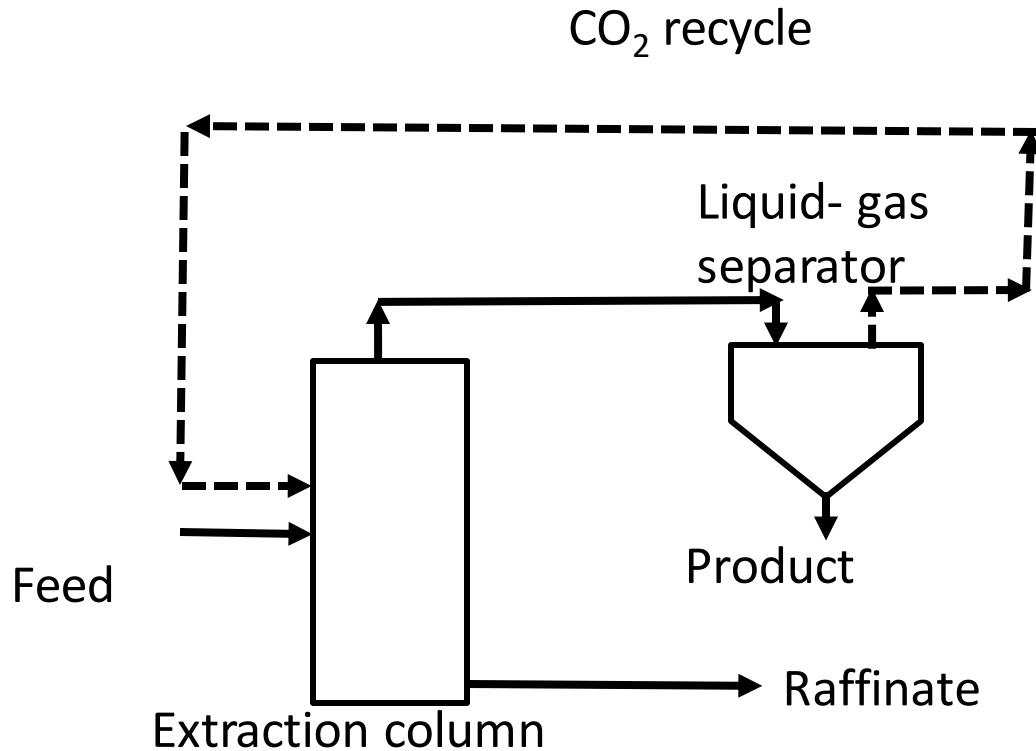


- The use of pervaporation for butanol extraction is based on High selective permeation and hydrophobicity of butanol through the hydrophobic membrane

Adapted from

J. Chem. Technol. Biotechnol. 80:603-29(2005).

Representation of butanol recovery by supercritical fluid extraction

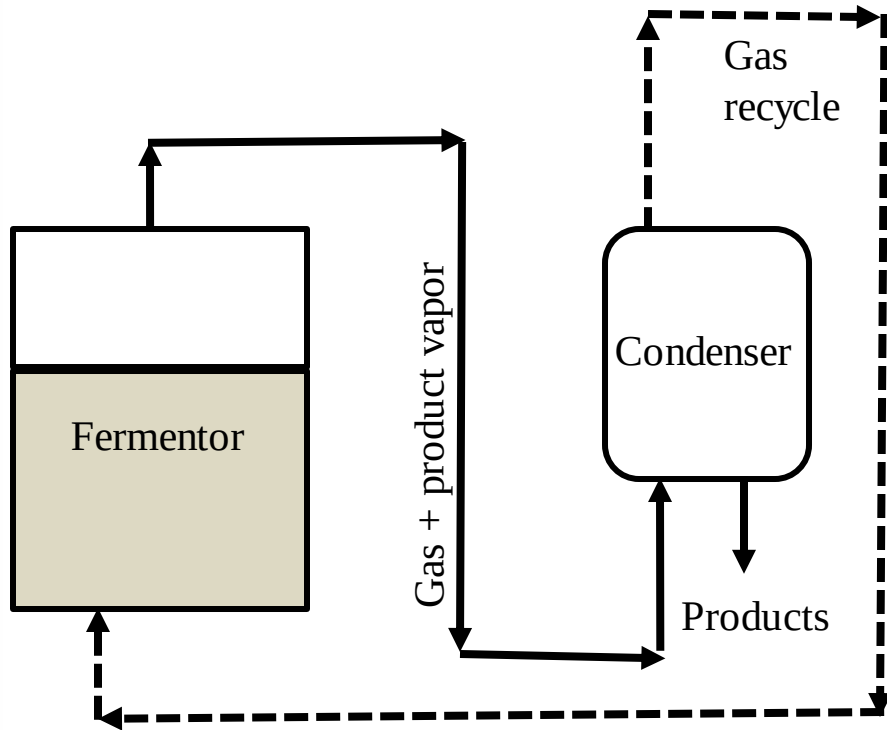


Adapted from

J. Supercrit. Fluids 15:245-52 (1999)

- Supercritical fluids, having both liquid-like and gas-like properties, can dissolve organic materials efficiently.
- Water above its critical temperature ($T_c > 374^\circ\text{C}$) and critical pressure ($P_c > 22 \text{ MPa}$) is called SCW.
- Similarly, CO₂ above its critical temperature ($T_c > 30.95^\circ\text{C}$) and critical pressure ($P_c > 7.38 \text{ MPa}$) is known as SCCO₂.

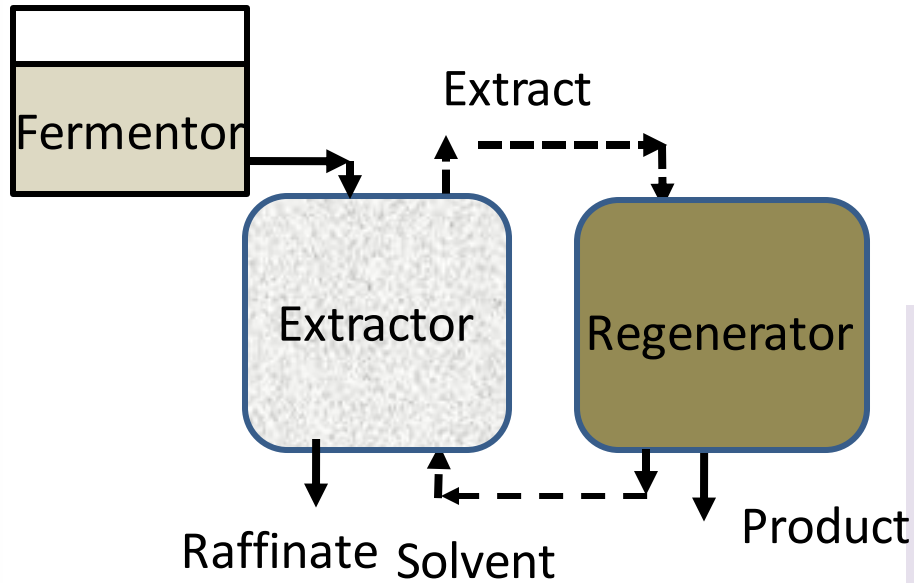
Representation of butanol recovery by gas stripping



- In principle, gas can be purged into the fermentor through a rotating shaft and the volatiles are condensed and recovered from the condenser.
- As the butanol fermentation is anaerobic, extreme care should be taken to avoid the entry of O_2 into the fermentation medium through gas stripping.
- Beneficial in its simplicity, cost-effectiveness, non-toxicity, no fouling or clogging due to the presence of biomass or cells.

(Adapted from Ezeji, *Chem. Rec.* 4:305-14)

Representation of butanol recovery by liquid-liquid extraction



(Adapted from Vane, 2008)

Biofuels, Bioprod. Bioref. 2:553-88

- Acetone, butanol and ethanol are separated by an extracting solvent and further recovered through back-extraction by another extracting solvent or via distillation.
- Extractants explored for butanol recovery include corn oil, polyoxyalkylene ethers, vegetable oil, hexanol, aromatic hydrocarbons, ketones, alkanes, esters, dibutyl phthalate, decanol and oleyl alcohol, crude palm oil and biodiesel

- It relies on the differences between the distribution coefficients of the solvents.

Representation of butanol recovery by distillation

- Distillation is a traditional method for butanol recovery from the aqueous fermentation broth.
- Distillation requires high energy as butanol has a boiling point (117.7°C) greater than that of water.
- A heterogeneous distillation, especially involving an azeotrope is used to separate butanol from water mixture.

B.P. of n-butanol 117.8°C , water 100°C , mixture 92.4°C (55 % butanol)



Advantages and limitations of butanol recovery technologies

Recovery technique	Advantages	Limitations	Energy requirement (MJ/kg)
Adsorption	(i) Easy operation. (ii) Less energy intensive.	(i) Low selectivity. (ii) High material cost. (iii) High adsorbent regeneration cost.	1.3-33
Distillation	Traditionally used. Less infrastructure requirement.	High operational cost due to low concentration of butanol. Highly energy intensive.	-



Advantages and limitations of butanol recovery technologies

Recovery technique	Advantages	Limitations	Energy requirement (MJ/kg)
Gas stripping	(i) High efficiency. (ii) Reduced butanol toxicity. (iii) Easy operation. (iv) No fouling.	Low selectivity. Low efficiency.	14-31
Liquid-liquid extraction	(i) Less energy intensive. (ii) High selectivity. (iii) High efficiency.	(i) High operational cost. (ii) Toxicity of extractant (iii) Emulsion formation	7.7-26



Advantages and limitations of butanol recovery technologies

Recovery technique	Advantages	Limitations	Energy requirement (MJ/kg)
Pervaporation	Selective removal of solvents. Less energy intensive. High flux	(i) High membrane cost. (ii) Vulnerable to temperature-sensitive compounds and cells.	2-145
Supercritical fluid extraction	(i) Cost-effective. (ii) Recyclable.	(i) Needs more research.	-



Lignocellulosic biomasses/ wastes and microbial strain used for butanol production

Feedstock	Bacteria
Aspen wood, Corn stover, Pinewood	<i>Clostridium acetobutylicum</i> P262
Bagasse, Rice straw	<i>Clostridium saccharoperbutylacetonicum</i> ATCC 27022
Barley straw, Wheat straw, Switchgrass	<i>Clostridium beijerinckii</i> P260
Corn fiber	<i>Clostridium beijerinckii</i> BA101
Pinewood, Wheat straw, Timothy grass	<i>Clostridium beijerinckii</i> B-592
Wheat straw	<i>Clostridium acetobutylicum</i> IFP 921



Thanks...

