Course Notes: BEE 478/578 Biofuel Feedstocks and Production

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Course Topics

Topic 1. ***Overview of biobased economy:*** Introduction to biofuels, available technologies introduction to biorefinery concept, bioethanol with emphasis on systems analysis and sustainability, (1 lecture)

Topic 2. ***Feedstocks:*** Types of feedstocks based on composition; chemical and physical properties; starch, cellulose, hemicellulose and lignin composition. (2 lectures)

Topic 3. ***Feedstocks assessment:*** An overview of issues involved in selection of feedstocks based on suitability, availability, sustainability and economic potential. (2 lectures)

Topic 4. ***Fermentation technologies for ethanol production:*** An overview of microbes used in biofuels production with special emphasis on yeast, enzymes, effect of process conditions and a summary of analytical techniques used. (3 lectures)

Topic 5. ***Ethanol production from starch rich feedstocks:*** Unit operations, SSF, distillation and post processing and utilization of coproducts. (3 lectures)

Topic 6. ***Thermochemical technologies for bioprocessing for fuels and chemicals:*** An overview of thermochemical technologies. (2 lectures)

Topic 7. ***Ethanol production from cellulosic feedstocks:*** Pretreatment technologies, hydrolysis, fermentation, and post processing and utilization of coproducts. (5 lectures)

Topic 8. ***Biobutanol production:*** Introduction to biobutanol production. (1 lecture)

Topic 9. ***Anaerobic Digestion***: Introduction and overview (2 lectures)

Topic 10. ***Other Bioproducts and Microbial Fuel Cells***: Introduction and overview (2 lectures)

Topic 11. ***Systems Analysis:*** Introduction to process modeling and economic analysis. (2 lectures)

Topic 12. ***Systems Analysis:*** Introduction to life cycle analysis using GREET. (2 lectures)

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Topic 1: Overview of biobased economy: Introduction, bioethanol, emphasis on systems analysis and sustainability.

- More than 80% of the world energy is derived from fossil fuels (oil, coal and natural gas).
- Available renewable energy course (solar and wind) exceed the global energy needs by orders of magnitude. However, only some fraction of available renewable energy sources are currently economically viable.
- All sources of energy are not same. Characteristics of energy sources that determine its usability are quality, energy density, shelf life and safety.
- Energy is the real currency of economies. In general, it is observed that per capita energy use is linearly correlated with per capita GDP around the world.
- Most of the newly developed/developing countries have large populations and relatively medium human development index values. In conjunction with the previous point this implies that there is a growing pressure on access to fossil fuels.
- Biofuels require agricultural land and large amounts of water to grow.
- Land and water are two of the important limiting natural resources.
- Nitrogen and phosphorous are two important macronutrients.
- Nitrogen fertilizer production involves use of large amounts of fossil fuels (one kg of urea requires 42 MJ of energy though natural gas).
- Phosphorous ore is mined just like coal and current projections on phosphorous availability indicate a peak phosphorous availability around 2030.
- Global climate change is expected to result in increasingly erratic rainfall, loss of biodiversity, ocean acidification, loss of fertile lands due to soil erosion and rising sea levels.
- Our dependency on fossil fuels extends not only to fuels but also to nitrogen fertilizers, plastics and chemicals. A bioeconomy must address challenges of sustainable producing these products from biomass.
- Technologies for biomass conversion are divided into five platforms: Sugars, thermochemical , lipid, biogas and bioproducts.

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Topic 2: Feedstocks: Types of feedstocks based on composition; chemical and physical properties; starch, cellulose, hemicellulose and lignin composition.

- Photosynthesis in plants is of three types: C3, C4 and CAM. Most plants including rice and wheat have C3 type of photosynthesis, while C4 photosynthesis is found in corn, sugarcane and other summer plants. CAM photosynthesis is common in plants that grow in deserts and other arid regions such as cactus and pineapple. C4 plants have higher water use efficiency compared to C3 plants.
- Starch is synthesized in plants by two classes of enzymes: Granule bound and soluble starch synthases. Amylose is a linear polymer of glucose connected by α 1→4 bonds and has a DP in the range of 300-5000. Amylopectin is a branched polymer connected by α 1→4 bonds (linear) and α 1→6 bonds (branches).
- Cellulosic biomass consists of three major polymers: Cellulose, Hemicellulose and Lignin. The primary cell wall in plants is made of cellulose while the lignin deposition occurs in secondary cell wall.
- Cellulose is synthesized by terminal complexes in the plasma membrane of plant cells. Cellulose is a homopolymer of glucose connected by β 1→4 bonds. Structurally, the repeating unit of cellulose is cellobiose, a disaccharide of glucose. Cellulose occurs in the form of elementary fibrils consisting of 36 chains of glucose. The elementary fibrils joint to form microfibrils which in turn form macorfibrils. There are six polymorphs of cellulose based on the structure of the cellulose fibrils. Type Iα and I_β are found in nature in bacteria and plants respectively while Type II is the most thermodynamically stable form.
- Hemicellulose is a heteropolymer of pentoses (xylose and arabinose), hexoses (glucose, galactose, and mannose) and other minir constituents (acetic acids, glucuronic acid and ferulic acid). Hemicellulose has a xylose backbone with significant substitution in the side chains by other monomers.
- Lignin is a racemic heteropolymer of three hydroxycinnamyl alcohol monomers (C9) differing in their degree of methoxylation: p-coumaryl, coniferyl and sinapyl alcohols They produce p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) phenylpropanoid units when incorporated into lignin polymer. Properties of lignin are dependent on the G:S:H ratio. Higher G:S ration in lignin makes it difficult to degrade compared to lower G:S ratios.
- Chain length of cellulose elementary fibrils, composition of hemicellulose and lignin are determined by the biomass type and environmental conditions during the biomass growth.

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Topic 4: Fermentation technologies for ethanol production: An overview of microbes used in biofuels production with special emphasis on yeast, enzymes, effect of process conditions and a summary of analytical techniques used.

- *Saccharomyces cerevisiae* is a versatile yeast used in almost all ethanol fermentations. It is a eukaryotic, unicellular fungi that reproduces by budding. *S. cerevisiae* is capable of both aerobic and anaerobic respirations and utilizes most hexoses and disaccharides such as maltose. It does not have the capability to ferment higher oligosaccharides of glucose or pentoses.
- Nutrient requirements of *S. cerevisiae* include:
  - Water : >15% w/w
  - Carbon source: mono and disaccharides (sucrose, glucose, fructose, maltose)
  - Nitrogen source: Inorganic nitrogen (as urea, ammonia), small chain peptides and amino acids (from protein degradation)
  - Lipids/oxygen: Lipids or oxygen for lipid production. Lipids are integral components of cell membranes.
  - Micronutrients: Vitamins, inorganic ions.
  - pH: Yeast can tolerate a wide range of pH although 4.0-6.0 is optimum.
  - Temperature: Optimum temperature 5- 35°C
- Although aerobic respiration yields more ATP (36 ATP/glucose) compared to anaerobic fermentation (2 ATP/glucose), yeast prefer the anaerobic fermentation pathway when the glucose concentrations are >2g/L even in presence of oxygen. This phenomenon is known as Crabtree effect.
- Yeast also exhibit diauxic shift, which refers to sequential consumption of substrates.
- Genetic modifications of yeast by overexpressing the enzymes in the xylose metabolism can confer xylose fermentation capability However, the capacity has mostly been demonstrated only in laboratory scale and is yet to be commercialized.
- Enzymes act as biological catalysts and help in lowering the activation energy. They, just like any other catalyst do not change the equilibrium. All enzymes are proteins. Tertiary and quaternary structure of protein provide the functionality of the enzyme.
- Michaelis-Menten kinetics are commonly used to model the enzyme activity on a substrate. However this approach is not particularly effective in case of experimental conditions such as limited/ restricted mobility of enzymes, two phase reactions, enzyme is not limiting, allosteric regulation.
- Enzyme nomenclature: EC 3.2.1.X stands for Enzyme Commission 3(Hydrolases). 2(sugars). 1(glycoside hydrolases). Ex. EC 3.2.1.4 is a cellulase (Endo-1,4-β-D-glucanohydrolase).
- Types of enzymes:
  - Endo Enzymes: these enzymes act on the inside of the polymer chains. In general these are non-processive enzymes.
  - Exo Enzymes: These enzymes act from the ends of the polymer chains. In general these are processive enzymes.
  - Processive Enzymes once attached to the polymer chain continue hydrolysis of subsequent bonds until the end of the polymer chain is reached.
  - Non Processive Enzymes once attached to the polymer chain perform only one hydrolysis and desorb from the polymer chain.
- Amylases: Amylases are enzymes that hydrolyze starch.
  - α-amylase (EC 3.2.1.1): An endo enzyme, hydrolyzes starch and produces oligosaccharides (dextrins).
  - β-amylase (EC 3.2.1.2) 1,4-α-D-glucan maltohydrolase: An exo enzyme that acts on starch

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to release maltose.
    - γ-amylase (EC 3.2.1.3) Glucan 1,4-α-glucosidase/ glucoamylase/amyloglucosidase: An exo enzyme that acts on starch to release glucose
- Pullanases: Pullanazes are debranching enzymes that act on α 1→6 bonds in starch. Type I pullanases only act on α 1→ 6 bonds while type II pullanases in addition to α 1→6 bonds also act on α 1→4 bonds with a reduced efficiency.
- Three mechanisms of cellulose degradation in nature:
    - Free cellulose mechanisms ex. *Trichoderma reesei* (aerobic fungi)
    - Cellulosomes (cellulases with a carbohydrate binding module, CBM) ex. *Clostridium thermocellum* (anaerobic bacteria)
    - Cellululases without CBM ex. *Fibrobacter succinogens* (anaerobic rumen bacteria)
- Cellulases: There are many different classes of cellulases that function synergistically to hydrolyze cellulose to glucose.
    - Endo Cellulases: Facilitate hydrolysis by exposing cellulose chains and disrupting the crystalline structure. ex. Endoglucanase
    - Exo cellulases: They further hydrolyze cellulose and yield cellobiose (a disaccharide). ex. Cellobiohydrolase I and II
    - Cellobiase: These enzymes hydrolyze cellobiose to glucose. ex. Betaglucosidase
    - Oxidative cellulases: "Depolymerize cellulose by radical reactions"
    - Cellulose phosphorylases: "Depolymerize cellulose using phosphates instead of water
- Cellulase classification: All cellulolytic enzymes All cellulolytic enzymes have two enzyme nomenclatures : EC 3.2.1.4 and 3.2.1.9. Cellulases are further classified based on their catalytic domain (CD) and carbohydrate binding module/domain(CBM/D). The CD classification is represented using Arabic numerals while CBM classification is indicated using Roman numerals.
    - There are about 70 structural families of glycosyl hydrolases (EC 3.2.1.X). Cellulases and hemicellulases are assigned to glycosyl hydrolase families:5,6,7,8,9,10,11,12,26,44,45,48,51,60 and 61. ex. *Trichoderma reesei* CBHI is *T. reesei* Cel7A.
    - There are more than 45 structural families of CBM. CBM I consisting of about 30 amino acids is found in fungal cellulases whicle CBM II with 120 amino acids is more common in aerobic bacterial cellulases while CBM III are found in cellulosomal scaffoldins. Many cellululases consist of multiple CBMs.
- Cellulose Hydrolysis: Endoglucanases (EG) act on internal chains to create additional chains. Cellobiohydrolases (CBHI and CBHII) cleave the -1,4 bonds creating cellobiose units. CBH I act from the reducing ends (R) while CBH II act from the non-reducing ends (NR). Betaglucosidase (BG) acts of the cellobiose/cellodextrins to produce glucose. Accessory proteins (AP) facilitate the hydrolysis through a currently unknown mechanism.
- *Trichoderma reesei* and *Aspergillus niger* are two commercially important cellulase producing fungi.

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Topic 5: Ethanol production from starch rich feedstocks: Unit operations, SSF, distillation and post processing and utilization of coproducts.

- Corn dry grind ethanol process is the largest commercial process for production of ethanol from corn. Currently about 20 billion liters of ethanol/year are produced using this process.
- Corn dry grind ethanol process consists of the following important unit operations:
  - Corn receiving and Grinding: Incoming corn is weighed, its moisture content is determined and is checked for the presence of mycotoxin producing fungi. The particle size of the corn is reduced using hammer mills. Typically a 2 mm sieve is used in the hammer mill.
  - Jet cooking and Liquefaction: The slurry of corn flour, process water and fresh make up water is heated rapidly by injecting steam directly into the process flow. Rapid rise of temperatures and shear forces completely gelatinize the starch. In the liquefaction tank, the starch is partially hydrolyzed by the action of α-amylase. Typical process conditions in liquefaction tank are 90 ºC, 6.5 pH and 90 min of residence time. In most industrial applications, the dosage of alpha amylase is split into before jet cooking (10 % of α-amylase dose) and after jet cooking (90 % of α-amylase dose). The dextrose equivalent of the liquified mash is between 12-22.
  - Simultaneous Saccharification and Fermentation: Liquified mash after adjustment of pH to ~4.5-5.0 is further hydrolyzed by the action of glucoamylase. Overall liquefaction and saccharification efficiencies are in the range of 70-90%. Glucose thus produced is utilized by the added yeast to produce ethanol with a typical fermentation efficiency of 95%. Since the saccharification and fermentation proceed simultaneously, the glucose concentrations do not increase significantly thus reducing opportunities for bacterial contamination. The SSF process typically is conducted at 30-33 ºC, 4.5-5.0 pH and 48-60 hr of residence time.
  - Ethanol recovery: First step of ethanol recovery consists of a three distillation columns: Beer boiler, rectification and stripper columns. In these distillations steps, beer (fermented corn mash) is distilled to recover a concentrated ethanol stream (~94-95% ethanol). Due to formation of ethanol-water azeotrope a second step consisting of molecular sieves is used to recover anhydrous ethanol.
  - Coproduct processing: Corn mash after ethanol removal is called whole stillage. Whole stillage is centrifuged to separate into thin stillage and wet grains. The thin stillage is concentrated in multiple effect evaporators to obtain syrup. The syrup is mixed with the wet graind and dried in a drum drier to obtain distillers dried grains with solubles (DDGS). In some cases, the syrup is directly sold as cattle feed additive to minimize drier loads and the dried wet grains are knows as distillers dried grains (DGS).
- Water and ethanol form a positive azeotrope that precludes use of a simple distillation for complete separation of ethanol in corn dry grind ethanol process.
- Molecular sieves are used in a pressure swing process to separate the anhydrous ethanol from ethanol-water mixture (95% ethanol) after two distillation steps. Commercial molecular sieve used in ethanol dehydration has pores of 3Å size (water molecule 2.8Å, ethanol 4.4Å). It is made by partial substitution of sodium ions with potassium ions in zeolite.
- On an average one bushel (25.4kg) of corn produces 10.2L (2.7 gal) of ethanol, 8.2 kg of CO2 and 8.2 kg of DDGS.
- DDGS has high fiber content (>10%) and is therefore used mostly in cattle rations and its use in swine and chicken rations is limited.
- Technologies such as dry degerm defiber, quick germ quick fiber, enzymatic milling are used to modify the conventional dry grind corn process to recover germ, pericarp fiber and endosperm fiber from the front end of the dry grind ethanol plants.

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Topic 6: Technologies for bioprocessing for fuels and chemicals: An overview of thermochemical technologies.

- Van Krevlen diagram (oxygen: carbon ration on x-axis and hydrogen: carbon ratio on y-axis) is used to compare different types of fuels. Fuels with low O:C ratio have high calorific value.
- Four major thermochemical conversion processes are: Combustion (burning biomass in stoichiometrically equal/excess oxygen), gasification (partial oxygen, low/high moisture), pyrolysis (no oxygen, low moisture) and hydrothermal liquefaction (no oxygen, high moisture).
- Main products of gasification are low/medium/high calorific synthesis gas consisting of a mixture of H_2, CO, CO_2, H_2O, N_2 and other gases in small fractions. The calorific value of the product gas can be varied by choosing appropriate oxidant (air, steam, oxygen, air/steam, oxygen/steam).
- Two main classifications of gasifiers are fixed bed and fluidized bed gasifiers. Fixed bed gasifiers are further classified into updraft (counter-current) and downdraft (cocurrent) gasifiers.
- Synthesis gas from gasifier is cleaned to remove tars, nitrogen, sulfur and alkali compounds using hot/cold cleaning method. The cleaned syn gas can be directly be used in internal combustion engines or further processed into liquid fuels using Fisher-Tropsh process.
- Pyrolysis is the heating of biomass in absence of oxygen usually conducted at 400-600 ºC. The main products of pyrolysis are biooil, char and gases. The proportion of these products can be controlled by regulating the temperature, pressure and feedstock characteristics.
- There are three types of pyrolysis: Conventional, fast and flash pyrolysis. The type of pyrolysis is defined by the solid residence time, heating rate and reaction temperature. Acceptable particle size of feedstock is determined by the type of pyrolysis.
- A typical fast pyrolysis process produces 75% liquid, 12% char and 13% gases as products.
- High moisture content (20-30% w/w), organic acids (10-15%w/w) and high oxygen content (35-40% w/w) are some of the underlying causes for undesirable properties of biooil such as low shelf life, corrosiveness, and increased visocsity during storage.
- Physical treatments (filtration, emulsification with other hydrocarbons, fractionation) and chemical treatments (esterification, catalytic deoxygenation/hydrogenation, thermal cracking, syngas production/gasification) are some of the approaches to improve the properties of biooil.
- Hydrothermal liquefaction (HTL) process is heating of high moisture feedstocks in absence of oxygen. Temperatures and pressure used in the process are around the critical point of water (373.95 ºC and 22.064 MPa). Reducing dielectric constant of water and increasing hydronium ion concentrations with increasing temperature allows water to solvate small organic molecules and enhance acid-catalyzed reactions. Solvent properties of water around 300-350 ºC are similar to acetone at room temperature.
- One of the major advantages of HTL process is that feedstocks with high moisture content can be used and the resultant streams are completely sterile.
- The yield of biooils in HTL process can be improved using homogeneous (ex. Na_2CO3) or heterogeneous (ex. Ni and Ru metals and alloys) catalysts. Similar to pyrolysis biooil, the HTL biocrude also must be upgraded to enhance its usability.

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Topic 7: Ethanol production from cellulosic feedstocks: Pretreatment technologies, hydrolysis, fermentation, and post processing and utilization of coproducts.

- Cellulosic ethanol from non-food feedstocks such as agricultural residues, dedicated energy crops such as switch grass, miscanthus, poplar, aspen, municipal solid wastes and other feedstocks is often called 'second generation biofuels'.
- A generic cellulosic ethanol process consists of the following important steps:
  - Cleaning and size reduction: Biomass is cleaned of debris such as sticks, rocks, soil and any metal objects. Knife mills are used to reduce the particle size of the incoming biomass. Knife mills are preferred for size reduction since cellulosic biomass is fibrous in nature.
  - Pretreatment: Primary goal of any pretreatment process is to facilitate enzyme action by making the substrate available. Pretreatment processes are critically dependent on type of feedstock.
  - Ideal pretreatment removes the barriers to effective hydrolysis, preserves sugars, minimizes inhibitor formation, is independent of the feedstock particle size, minimizes energy and resource use, is cheap and safe.
  - There are many types of pretreatment processes classified into physio-chemical (steam explosion, liquid hot water, ammonia fiber expansion AFEX, ionic liquids etc.) and chemical pretreatment (dilute acid, dilute alkali, organosolv etc.) methods. Of these Dilute acid (using 0.5-3% H_2SO_4), liquid hot water and steam explosion are most commonly used pretreatment methods. In general the most pretreatments are conducted in the temperature range of 160-200 °C with a residence time between 10-30 min. Alkali based pretreatment methods such as AFEX process have lower temperature (90 °C) requirements. Pretreatment methods using lime with aeration is different from above mentioned methods as it is conducted at near ambient temperatures (25-60 °C) and pressures (1 bar) with long residence times (2 weeks-2 months).
  - Severity index is an indicator of the combined effect of temperature (T, °C), reaction time (t, min). This is specific for a particular feedstock and specific pretreatment method.

$$CS = \log_{10}\left(t\, e^{((T-100)/14.75)}\right)$$

A modification to the above definition of the severity factor to incorporate the effects of pH is called combined severity factor and is defined as follows:

$$mCS = \log_{10}\left(t\, e^{((T-100)/14.75)}\right) - |pH-7|$$

  - Increasing severity factor beyond the value for maximum sugar release results in formation of inhibitors.
  - More than 70 different cell growth inhibitors have been detected in pretreated hydrolyzate. Furfural and hydroxy methyl furfural (HMF) formed from the degradation of xylose and glucose respectively, lignin degradation products such as cinnamaldehyde, p-hydroxybenzaldehyde and syringaladehyde and hemicellulose degradation products such acetic, formic, glucuronic and galacturonic acids are important inhibitors. The inhibitors are classified into aliphatic acids, furan compounds and aromatic aldehydes. The action of inhibitors is primarily through chemical interference with cell maintenance functions, inhibition of ethanol production pathways and osmotic effects on cells.
  - Suppression/removal of inhibitor effects can be accomplished by detoxification or bioreduction strategies. Evaporation, extraction with organic solvents, ion exchange resins, adsorption on activated charcoal, alkaline detoxification (overliming), enzyme detoxification are some of the detoxification strategies. Bioreduction strategies include strain selection, long/short term adaptation, targeted genetic modification and improved process design. Of these approaches, the overliming process, in which the pH of the pretreated hydrolyzate is increased to 10-12pH and subsequently reduced to 5.5 pH using

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H_2SO_4 or sodium sulfite (more effective) is one of the best known methods for detoxification although the exact detoxification mechanism is not completely understood. Microbial detoxification is focused mostly on the lignolytic enzymes such as laccases, Mn peroxidases, heme peroxidases, blue copper oxidases and phenol oxidases produced by white rot, brown rot and soft rot fungi. Although the microbial detoxification methods are effective, they are not commercially practiced due to unavailability of lignolytic enzymes at industrial scales.

- Enzymatic Hydrolysis and Fermentation: after pretreatment, the solids stream consisting mainly of cellulose and lignin is enzymatically hydrolyzed using a synergistically acting mixture of cellulase enzymes. There are two general schemes of fermentation followed in cellulosic ethanol processing. In the first scheme, called separate saccharification and fermentation, the glucose released by enzymatic hydrolysis is fermented separately from the pentose rich stream obtained from the detoxified liquid hydrolyzate. This approach allows for optimization of pentose and hexose fermentations separately. In the second scheme, the pentose rich stream is combined with simultaneous saccharification and fermentation of hexose sugars and is therefore called simultaneous saccharification and cofermentation process.
- Ethanol Recovery Technologies: The ethanol recovery technologies can be divided into end-of-pipe or slip stream alcohol recovery technologies. In the end-of-pipe technologies, exemplified by distillation process, ethanol is recovered after the completion of fermentation while in the slip stream technologies, ethanol is simultaneously recovered from a slip stream during fermentation. Distillation, gas/steam stripping, liquid-liquid extraction, adsorption and pervaporation are some of the technologies than are/can be used for ethanol recovery. Based on the energetics of distillation, >5 wt% ethanol concentration in the feeds stream is required to minimize the energy use in distillation. The values for other technologies varies from >2 wt% to >5 wt% based on the design and operating parameters.

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Topic 8: Biobutanol production

- Butanol is a 4-Carbon Alcohol (Most common forms are normal butanol (n-buOH) and iso-butanol (i-buOH)
- Acetone, Butanol, Ethanol (ABE) Process
- Advantages of biobutanol: 1. Higher energy content than ethanol 2. Less hydrophilic than ethanol 3.More compatible with oil infrastructure 4. Lower vapor pressure and higher flash point than ethanol 5. Less corrosive 6. n-butanol works well with diesel 7. Both n-buOH and iso-buOH have good fuel properties
- Why commercial butanol production is challenging? 1. Butanol yield from glucose is low, between 22-26%, 2. Butanol concentration in the fermentation rarely exceeds 1.5%, 3. Butanol at a concentration of 1% can significantly inhibit microbial cell growth, 4. Butanol fermentation is biphasic, 5. High substrate cost and, 6. High energy inputs required to recover butanol from dilute streams
- An integrated batch process resulted in the production of 21.4 g/L AB with a productivity of 0.31 g/L.h.
- In an integrated fed-batch reactor 430.0 g/L total cellulosic sugars were used thus producing 192.0 g/L total AB
- Major integrated product recovery systems for butanol production: 1. SSFR_Simultaneous saccharification, fermentation and recovery, 2. Gas Stripping (N2 and/or fermentation gases - CO2 & H2), 3. Cell recycle, 4. Pervaporation (use of selective membranes – silicone, silicone-silicalite, polypropylene, liquid membranes), 5. Vacuum fermentation, 6. Liquid-liquid Extraction (uses solvents e.g. oleyl alcohol, dibutyl phthalate, and dodecanol), 7. Perstraction (Combination of solvents and membranes)
- Considerations for choosing an extractant: 1. Non-toxicity of the extracting solvent to the fermenting microorganism, 2. High partition coefficient of extracting solvent, 3. Low aqueous solubility, 4. Cost of extracting solvent, 5. Non-hazardous to the personnel or environment, 6. Ease of extracting solvent Regeneration
- Number one problem with Liquid-Liquid extraction: Formation of emulsions and cell aggregation at the liquid – liquid interface (rag layers) extending to the whole extracting solvent

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Topic 11: Systems Analysis-Techno-economic Analysis

- The techno-economic analysis (TEA) is used to assess the technical and economic viability of a process, and to identify the optimal unit processes and performance conditions considering ***both*** technical and economic factors.

- One of the first steps of TEA is to define the scope of the analysis and identify the types of estimate which can be classified as:
  - Order of magnitude estimate: ±10 to 50% accuracy
  - Study estimate (factored estimate): ±30%
  - Preliminary estimate (budget authorization estimate): ±20%
  - Definitive estimate (project control estimate): ±10%
  - Detailed estimate (firm or contractor's estimate): ±5%
- Basic Steps in TEA: Base Design, Material and energy balances, optimization of the process, estimation of direct costs, indirect cost, fixed capital costs, operational expenses and cash flow analysis to determines the net present value, internal rate of return and payback period.
- The internal rate of return (IRR) is equal to the rate of return when the net present value (NPV) is equal to zero. The IRR indicates the efficiency of the enterprise to return profits and if the IRR is greater than the cost of capital (i.e., cost to invest the money elsewhere in other profitable venture with a similar financial risk profile) the project is accepted.

$$\mathrm{NPV} = \sum_{n=0}^{N} \frac{C_n}{(1+r)^n} = 0$$

Where, C_n refers to the cash flow during the year n, for a total of N years. When the value of IRR is set to a defined discount rate in the above formula, the resulting value is the NPV for the project. The discount rate (i) is opportunity cost of the capital.

$$\mathrm{NPV} = \sum_{n=0}^{N} \frac{C_n}{(1+i)^n}$$

- The payback period refers to the time required to recover the investment from the project. The payback period is always less than the project life time for economically viable projects. If all other factors are equal, projects with shorter payback period are selected.

$$\text{Payback period} = n^{-} + \frac{S_{n^-}}{C_{n^-+1}}$$

Where, n^- is the last period with a negative cumulative cash flow, S_{n^-} is the cumulative cash flow at the end of the time period n^- and C_{n^-+1} is the cash flow for the time period $n^- + 1$.

- TEA at the level of study/factored study estimates is performed using process modeling software such as Aspen Plus® and SuperPro Designer® among others.
- Data for individual process equipment and different scaling factors can be obtained from engineering handbooks such as Perry's chemical engineering handbook (Perry and Green, 1998), The engineer's cost handbook (Westney, 1997), RS means (RSMeans,2009) and online databases (Matche, 2013).

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Topic 12: Systems Analysis-Life Cycle Assessment

- Life Cycle Assessment (LCA) techniques are used to quantitatively compare the impacts of various processes, products and services on the environment. Methods to compare environmental impacts can be divided into process oriented and environmentally emphasized metrics. Process oriented metrics such as a typical LCA are useful in assessing competing technologies.
- LCA is used to assess the potential environmental impacts and resources used throughout a product's entire life cycle: from raw material acquisition, via production and use phases, to waste management (ISO, 2006).
- It is important to note that the LCA is not a risk assessment, i.e., it does not provide any information on the inherent risk associated with a particular product/technology. LCA also does not provide any information on profitability of the process/product.
- There are two variants of LCA which answer different questions: *attributional LCA* and *consequential LCA*.
    - aLCA: What are the ***total*** emissions from the process during the life cycle of the product?
    - cLCA: What is the ***change*** in total emissions from the process during the life cycle of the product?
- LCA consists of four distinct steps, namely: 1) goal and scope definition, 2) inventory, 3) impact assessment, and 4) interpretation. Often these steps are interlinked and are iterative. Methodology for LCA is standardized in the International Organization for Standardization (ISO) 14040-14044 (ISO, 2006).
- Based on the differences in the goals and scope of an LCA, they can be classified as cradle to cradle, cradle to grave or cradle to gate LCA.
- The ISO 14040:2006 definition of the functional unit states: "Functional unit defines the quantification of the identified functions of the product. The primary purpose of a functional unit is to provide a reference to which inputs and outputs are related."
- Currently, some of the commonly available software available are OpenLCA, Simapro, GaBi, Sustainable Minds, Enviance System, Economic Input-Output LCA (EIOLCA), Eco-LCA and Greenhouse gas and Regulated Emissions for Transportation (GREET). While Simapro is one of the most commonly used LCA software, OpenLCA is an open source software with comparable features.

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