MANIPAL INSTITUTE OF TECHNOLOGY
MANIPAL
(A constituent unit of MAHE, Manipal)

VI SEMESTER B.TECH. ENDSEMESTER EXAMINATION MAY 2022

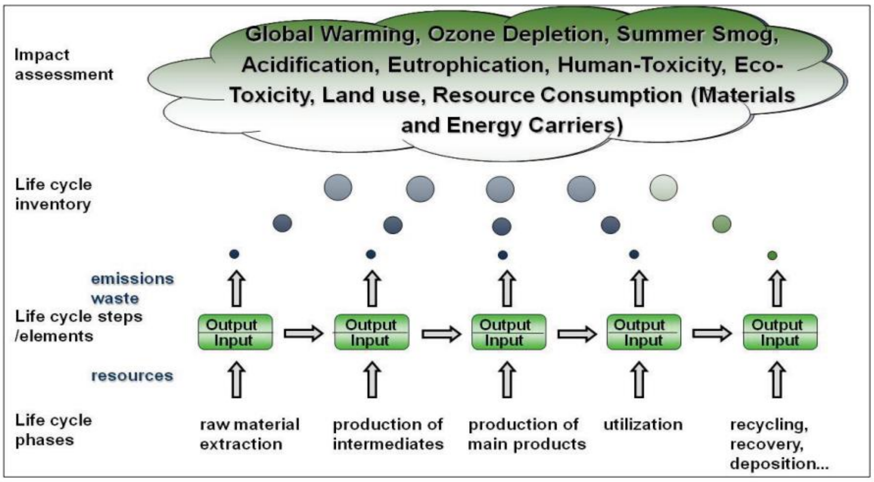
SUBJECT: INTRODUCTION TO BIOFUELS AND BIOPOLYMERS

[BIO 5052]

Date of Exam: 23-05-2022 Time of Exam: 10:00 AM to 1:00 PM Max. Marks: 50

Q. No.	Questions	Marks	CO	BLT
1A	What are Biofuels? List the classification of biofuels based on generation of products. List the merits and drawbacks of biofuels.	4	1	1
1B	Describe the general product life cycle, as done in LCA, with a detailed schematic.	3	1	2
1C	Mention and briefly describe the four main options to define the system boundaries used in life cycle assessment.	3	1	2
2A	Show the process flowsheet of the bioethanol production by fermentation process of starch feed stock. Choose any one stage/step and give a short description.	4	2	2,4
2B	Show the detailed process flow chart of biodiesel production from microalgae.	3	2	2,4
2C	Determine theoretically the gas composition (% carbon dioxide and % methane) when digesting protein ($C_5H_7O_2N$). Data: Buswell equation: $C_cH_hO_oN_nS_s$ + {(4c - h - 2o + 3n + 2s)/4} H_2O -----→ {(4c - h + 2o + 3n + 2s)/8} CO_2 + {(4c + h - 2o - 3n - 2s)/8} CH_4 + nNH_3 + sH_2S	3	2	3
3A	Explain in brief the working principle of two chamber microbial electrolysis cell for hydrogen production. Name the parameters which play an important role in determining the hydrogen yield in MEC.	4	3	2,3
3B	Distinguish between BOD and COD.	3	3	1
3C	What is the mechanism of action involved in the acidogenesis, acetogenesis and methanogenesis steps during the formation of biogas.	3	3	2,4
4A	Explain briefly the microbial production and biodegradability of polylactic acid. Enlist the applications of biopolymer polylactic acid.	4	4	2
4B	Differentiate between thermosetting polymers and thermoplastic polymers.	3	4	1

4C	Write a short note on Cellulose and Starch.	**3**	**4**	**1**
5A	How does the incorporation of additives and flame retardants in biopolymers affect their properties and applications?	**4**	**5**	**2**
5B	What are the necessary parameters that must be satisfied by a material to claim to be biodegradable?	**3**	**5**	**4**
5C	List the salient properties of bioplastics in comparison with synthetic plastics.	**3**	**5**	**4**
CO: Course Outcome; BLT: BLOOM TAXONOMY LEVEL: 1-Remember, 2-Understand, 3-Application, 4-Analysis, 5-Evaluation, 6-Creation				

<table>
<tr><th>Q. No.</th><th>Answer Keys</th><th>Marks</th></tr>
<tr><td>1A</td><td>A fuel manufactured either from or by fresh, living micro- or macro-organisms or a fuel made directly or indirectly from biomass.
<u>Classification</u>
First Generation Biofuels
Second Generation Biofuels
Third Generation Biofuels
Fourth Generation Biofuels
<u>Merits</u>
Biodegradability • Readily available feedstock • Environmentally and socially beneficial • Ensure energy availability • Extensive applications • Easy blending with petroleum-based fuel • Safe handling and transportation.
<u>Drawbacks</u>
Compete with food • Lead to the food vs. fuel debate • Growing of feedstocks requires large arable land and time • Agricultural inputs like fertilizer, herbicides, irrigation, and manpower required • Contribute the highest carbon footprint in comparison with other generations of biofuels.</td><td>4</td></tr>
<tr><td>1B</td><td>
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<tr><td>1C</td><td>Cradle to Grave: includes the material and energy production chain and all processes from the raw material extraction through the production, transportation and use phase up to the product's end of life treatment.
Cradle to Gate: includes all processes from the raw material extraction through the production phase (gate of the factory); used to determine the environmental impact of the production of a product.
Gate to Grave: includes the processes from the use and end-of-life phases (everything post production); used to determine the environmental impacts of a product once it leaves the factory.
Gate to Gate: includes the processes from the production phase only; used to determine the environmental impacts of a single production step or process.</td><td>3</td></tr>
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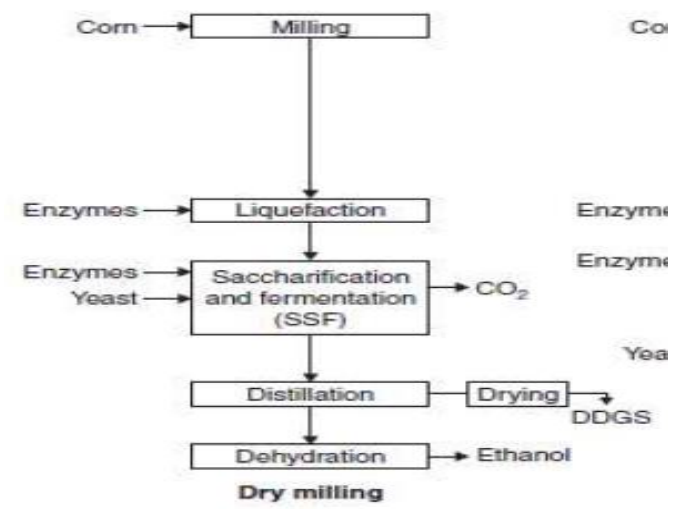
<tr><td>2A</td><td>
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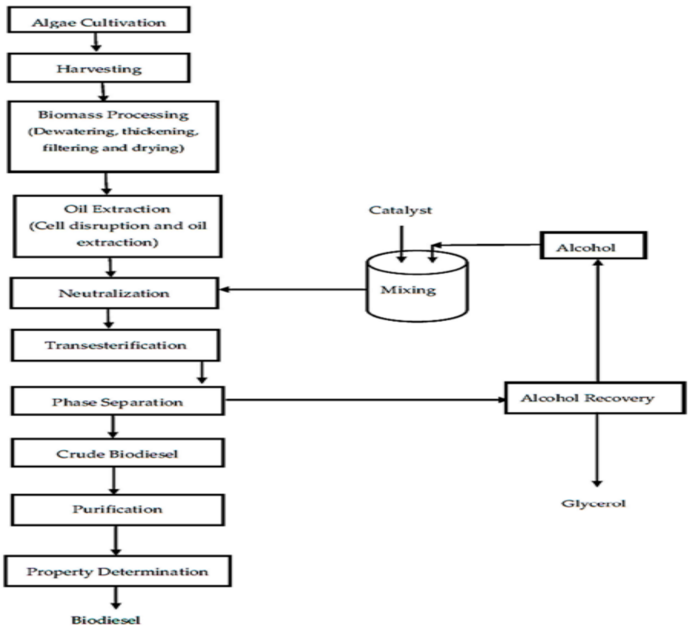
<tr><td>2B</td><td>
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<tr><td>2C</td><td>

From the Buswell equation: c=5, h=7, o=2, n=1 (s=0)
Note that in practice all ammonia (NH3) dissolves in the slurry. Therefore we only calculate CO2 and CH4
C5H7O2N + {(4x5-7-2x2+3x1)/4} H2O →
{(4x5-7+2x2+3x1)/8} CO2+ {(4x5+7-2x2-3x1)/8} CH4
C5H7O2N + 3 H2O → 2.5 CO2+ 2.5 CH4
The molar ratio for CO2 and CH4 is 2.5 : 2.5, thus the gas composition is 50% CO2 and 50% CH4
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<td>3A</td>
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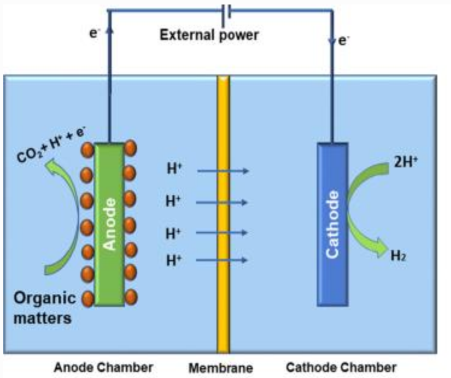
MEC technology is also known as biocatalysed electrolysis cells or electrofermentation. The MEC system has two electrodes, cathode and anode, which can either be placed in the same single chamber (single-chamber MEC) or be separately placed in two individual chambers (two-chamber MEC). In the two-chamber MEC, to separate the two chambers, commonly a proton exchange membrane is used. Other recently developed membranes include a charge-mosaic membrane, cation/anion exchange membrane and bipolar membrane. In the two-chamber MEC, the anode chamber is filled with the organic wastewater, while the cathode chamber can be filled with different solutions (like moderate acidified water, phosphate-buffered solution, bicarbonate buffers and salt solution. The main working process in both the MEC types is the same. Electrons get generated by the oxidation of organic matter in the anode, which are transported to the anode. Then, they are transported to the cathode where upon combining with protons, H_2 gets generated. In addition to a potential generated by microorganisms (− 0.300 V), MEC needs a small external potential of more than 0.110 V for the production of H_2. The external power source use of the battery is generally considered, but the use of renewable power generated from solar, wind, MFCs and waste heat can be seen.

Anode:CH3COOH+2H2O→2CO2+8e−+8H+Anode:CH3COOH+2H2O→2CO2+8e−+8H+

Cathode:8e−+8H+→4H2Cathode:8e−+8H+→4H2

Overall:CH3COOH+2H2O→2CO2+4H2Overall:CH3COOH+2H2O→2CO2+4H2

Many different substrates were found in use for MEC to produce H_2. Some common pure chemical substrates used are butyrate, glucose, acetate and glycol. However, different waste streams like poultry farming wastewater, domestic wastewater, waste activated sludge and industrial wastewater are used in MEC.



Two-chamber MEC

Raw materials, temperature, pH and operating voltage play an important role in determining the H_2 yield in MEC.
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<td>3B</td>
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Definition BOD: BOD is the amount of oxygen consumed by bacteria while decomposing organic matter under aerobic conditions. COD: COD is the amount of oxygen required for the oxidation of total organic matter in water.
Decomposition BOD: BOD is a biological oxidation process. COD: COD is a chemical oxidation process.
Test Procedure BOD: BOD is determined by incubating a sealed water under specific temperature sample for five days and measuring the loss of oxygen from the
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	beginning of the test. COD: COD is determined by incubating a closed water sample with a strong oxidant like potassium dichromate (K2Cr2O7) in combination with boiling sulfuric acid (H2SO4) under specific temperature for a specified period of time. **Time Taken for Determination** BOD: Five days are taken for the determination of the BOD. COD: COD measurement can be taken from few days.	

3C	**Acidogenesis**
	• Conversion of sugar monomers to pyruvate ($C_3H_4O_3$), Adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide (NAD) + hydrogen(H) (NADH) by central metabolic pathway (glycolysis)
	• Next pyruvate, amino acids to *primarily* acetate, propionate, butyrate, succinate, alcohols, CO_2 & H_2.
	• Short-chain organic acids (OAs) produced ➔ Acidogenesis.
	Acetogenesis
	• OAs produced by fermentation & Fatty Acids produced from hydrolysis of lipids are fermented to acetic acid, H_2 & CO_2 by acetogenic bacteria.
	• Syntrophic bacteria that oxidize OAs to acetate, H_2 & CO_2 rely on subsequent oxidation of H_2 by the next group of methanogens, to lower [H_2] & prevent end product inhibition.
	    • Syntrophic H_2 production favorable, only at very low H_2 partial pressure.
	• If methanogens bacteria are disrupted, this causes accumulation of H_2 ➔ inhibition of acetogenesis
	Methanogenesis
	2 distinct routes exist for CH_4 generation by 2 distinct microbial groups.
	– Lithotrophic H_2–oxidizing methanogens use H_2 as e^- donor & reduce CO_2 to CH_4: 1/3rd CH_4 produced this way.
	    • $4H_2 + CO_2 \rightarrow CH_4 + 2H2O$
	– Organotrophic acetoclastic methanogens ferment acetic acid to CH_4 and CO_2: remaining 2/3rd CH_4
	    • $CH_3COOH \rightarrow CH_4 + CO_2$
	– ≈ 85-90% of energy is converted in the form of CH_4 if complete conversion of carbohydrates (like glucose) to CH_4 occurs under anaerobic digestion.
		3

4A	Explain briefly the microbial production and biodegradability of polylactic acid. Enlist the applications of biopolymer polylactic acid. Bacterial fermentation is used to produce lactic acid from corn starch or cane sugar. Two lactic acid molecules undergo a single esterfication and then catalytically cyclized to make a cyclic lactide ester. PLA of high molecular weight is produced from the dilactate ester by **ring-opening polymerization**. Polymerization of a racemic mixture of L- and D-lactides usually leads to the synthesis of **poly-DL-lactide (PDLLA)** which is amorphous.	**4**

	APPLICATIONS • Woven shirts (ironability), microwavable trays, hot-fill applications and even engineering plastics (in this case, the stereocomplex is blended with a rubber-like polymer such as ABS). Acrylonitrile butadiene styrene • PLA is currently used in a number of biomedical applications, such as sutures, stents, dialysis media and drug delivery devices. The total degradation time of PLA is a few years. It is also being evaluated as a material for tissue engineering. • Because it is biodegradable, it can also be employed in the preparation of bioplastic, useful for producing loose-fill packaging, compost bags, food packaging, and disposable tableware. In the form of fibers and non-woven textiles, PLA also has many potential uses, for example as upholstery, disposable garments, awnings, feminine hygiene products, and diapers. • PLA is a sustainable alternative to petrochemical-derived products, since the lactides from which it is ultimately produced can be derived from the fermentation of agricultural by-products such as corn starch or other carbohydrate-rich substances like maize, sugar or wheat.	
4B	Differentiate between thermosetting polymers and thermoplastic polymers. ➢ If crosslinking extends throughout the network of polymer, then the final article is stable to heat and cannot melt and flow. They are called **thermosetting polymers** ➢ Most linear and branched polymers can be made to soften and take on new shapes by the application of heat and pressure; called **thermoplastic polymers.**	**3**
4C	Write a short note on Cellulose and Starch. ➢ **Cellulose** is a skeletal polysaccharide ubiquitous in the plant kingdom and one of the commonest naturally occurring crystalline polymers. ➢ It is usually in a fibrous form, and functions as the reinforcement for the amorphous lignin and hemicelluloses resulting in a composite woody structure. ➢ The primary structure of cellulose is essentially a regular unbranched linear sequence of 1→4 linked β-D-glucose. ➢ Neighbouring chains may form hydrogen bonds leading to the formation of microfibrils. ➢ Cellulose is the most abundant and renewable biopolymer comprising about 40% of all organic matter • **Starch** is a particular form of carbohydrate and is a biopolymer of anhydroglucose units linked by α→4 linkages. • It is one of the most abundant, naturally occurring biodegradable polymers made up mainly of two polysaccharides namely amylose (molecular weight of up to 2,000,000) and amylopectin (100- 400,000,000). • Amylose is a linear 1→4 linked α-Dglucan that occurs in the crystalline form in starch granules and amylopectin is an α-1,6-branched α-1,4 glucan polymer. • The amylose and amylopectin molecules are in an ordered arrangement within the starch granule and this gives crystallinity to the granule.	**3**

	• Starch granules exhibit hydrophilic properties and strong intermolecular association via hydrogen bonding due to the hydroxyl groups on the granule surface.	
5A	How does the incorporation of additives and flame retardants in biopolymers affect their properties and applications? **Additives:** • Processing aids and property improvers. • These additives are usually added in small quantities, and with the exception of the biocides, are unlikely to have any effect on the gross biodegradation of the polymer. • However, the selection of additives for biodegradable polymer systems should be undertaken with care to avoid compromising the biodegradability certification of the finished article. **Flame retardants** • The chemicals used to reduce the flammability of polymers are commonly chlorinated and brominated compounds (sometimes with antimony- based synergists) used as flame quenchers, and phosphorous compounds to improve char strength. • These are regarded as undesirable due to perceptions of their toxicity. Alumina trihydrate ($Al_2O_3.5H_2O$) releases its water of hydration when subjected to heat, and hence limits the propagation of combustion. • However it is added in large amounts to the polymer (50-60%), and may, at the upper limits of addition, compromise the biodegradability of the article.	**4**
5B	What are the necessary parameters that must be satisfied by a material to claim to be biodegradable? • Advantages on biodegradable polymer – Didn't leave traces of residual in the implantation – Regenerate tissue • Desirable properties are - greater hydrophilicity - greater reactivity - greater porosity **Most widely used** Polylactide (PLA), Polyglycolide (PGA), Poly(glycolide-co-lactide) (PGLA) **Applications** Tissue screws, suture anchores, cartilage repair Drug-delivery system	**3**

5C	List the salient properties of bioplastics in comparison with synthetic plastics. • Some are stiff and brittle – Crystalline structure → rigidity • Some are rubbery and moldable • Properties may be manipulated by blending polymers or genetic modifications • Degrades at 185°C • Moisture resistant, water insoluble, optically pure, impermeable to oxygen • Must maintain stability during manufacture and use but degrade rapidly when disposed of or recycled	**3**