Circular Economy opportunities of microalgal-based wastewater treatment: materials and energy recovery pathways

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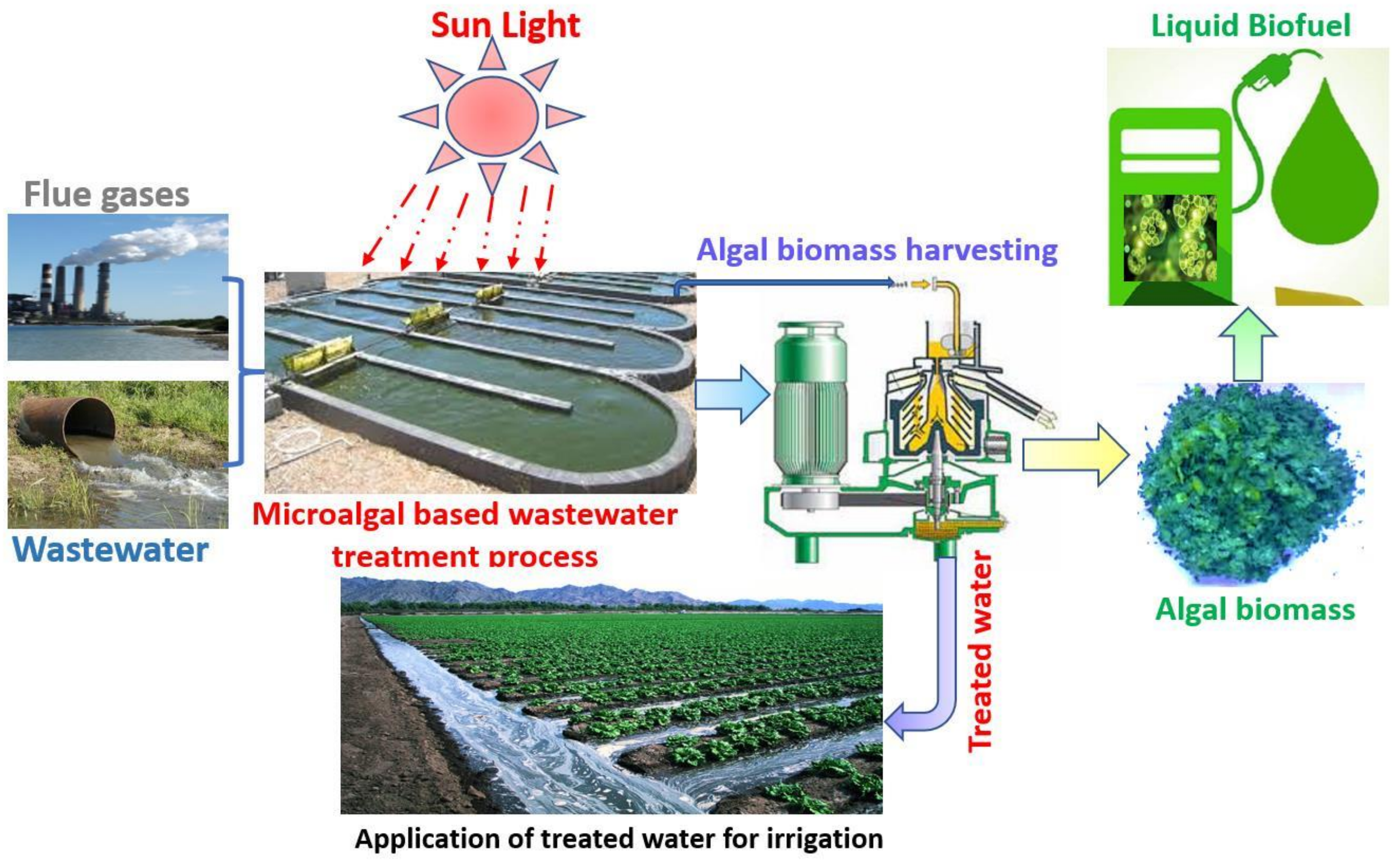
Microalgal-based wastewater treatment

- new class of nature-based, mixotrophic systems, where light and CO_2 are utilized in addition to the organic C by algal cultures
- algae-based systems can simultaneously remove organic matter, N, and P
- offer energetic advantages compared to traditional biological treatment systems, require smaller footprint than CWs, contribute to biofuel production and CO_2 emission mitigation

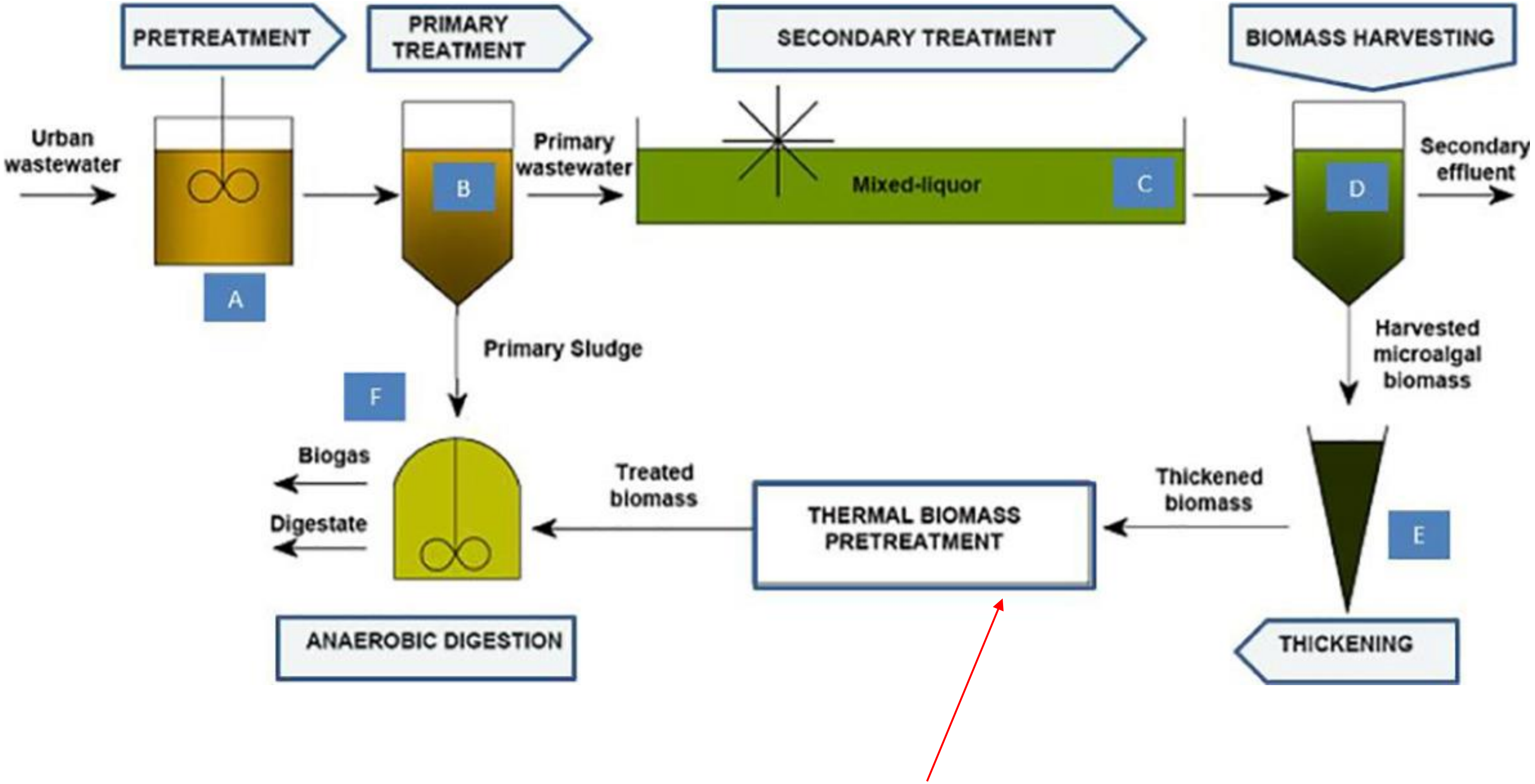


Microalgal-based wastewater treatment

- first studied in the 1950s, symbiotic relationship between microalgae and bacteria show capacity to protect algae from toxic compounds in wastewater, improve contaminants removal
- microalgae use CO_2 through photosynthesis, generated O_2 is used by heterotrophs to assimilate C, N, P
- CO_2 and inorganic N and P released by bacterial metabolism used by microalgae to assimilate significant amounts of nutrients: high demand for protein, nucleic acids, phospholipids
- lower cost compared to conventional biological treatment facilities: energy consumption is much lower (at least tenfold) compared to conventional WWTPs, around 0.02 kWh/m^3 treated
- algal biomass can generate considerable added value as feedstock in biorefineries, or other applications

Microalgal-based wastewater treatment

- one major drawback of algae-based systems is biomass harvesting and processing
- very small fraction (up to 0.05%) of dry weight in suspension, microscopic cell size, and negative surface charge, prevent biomass from agglomerating into easily harvestable particles, increasing the costs of final separation
- cost of algae biomass harvesting: up to 30% of total process expenses
- algal pond systems can become cost-effective when coupled with biorefinery or biofertilizer production: higher added value byproducts compared to energy recovery from algal co-digestion



(Issues with efficient algal dewatering and lipid extraction prior to AD)

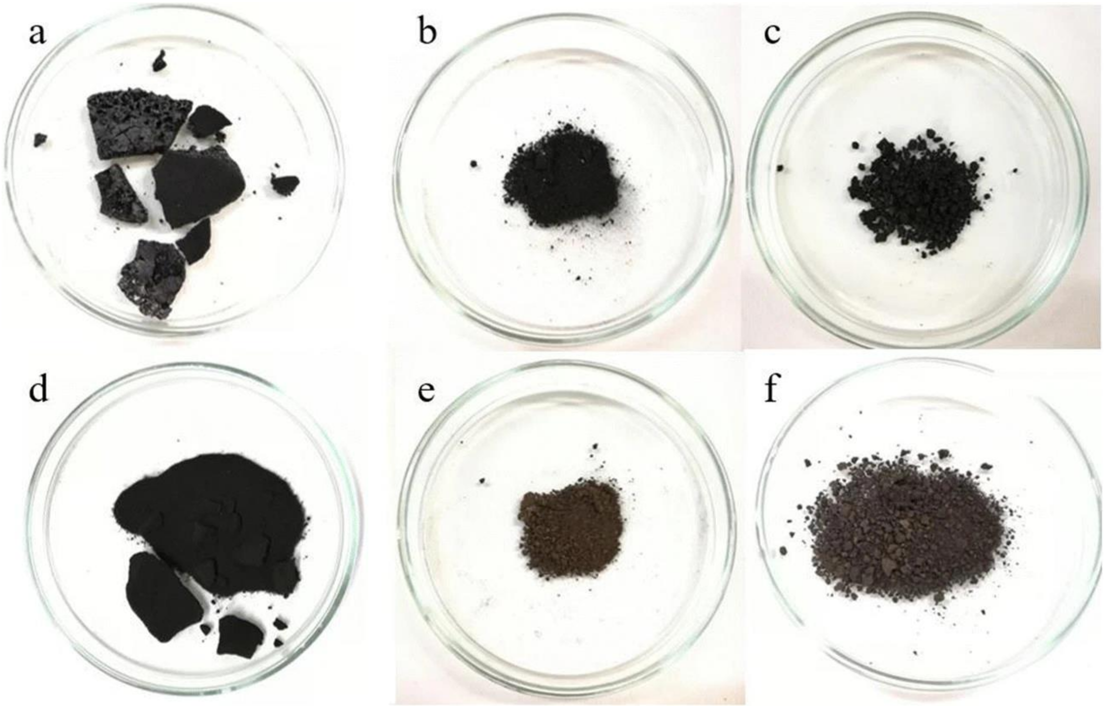
Biochar production from sewage sludge and microalgae mixtures

- one of the most interesting final products in wastewater-based circular economy: multitude of possible uses tested so far.
- combined activated sludge (AS)-microalgae generate potential issues of solid residue disposal practices (algae respond poorly to traditional drying)
- disposal solution consists of pyrolysation of mixed sludge/bioalgae matrices: generate material with multiple potential end uses
- ash content in WWTP sludge higher than in microalgae: adding even a small amount (15%) of microalgae to the mix positively contributes to improving of biochar energy content
- solvent oil pre-extraction from microalgae increases biochar yield

Feedstock	% ashes (800 °C)	% residues (char + ashes, 800 °C)
Microalgae *Chlorella*	13.7 ± 2.6	25.1 ± 1.4
Sludge WWTP	30.2 ± 1.8	36.2 ± 2.1
Mix A + S	24.4 ± 3.1	38.7 ± 1.9

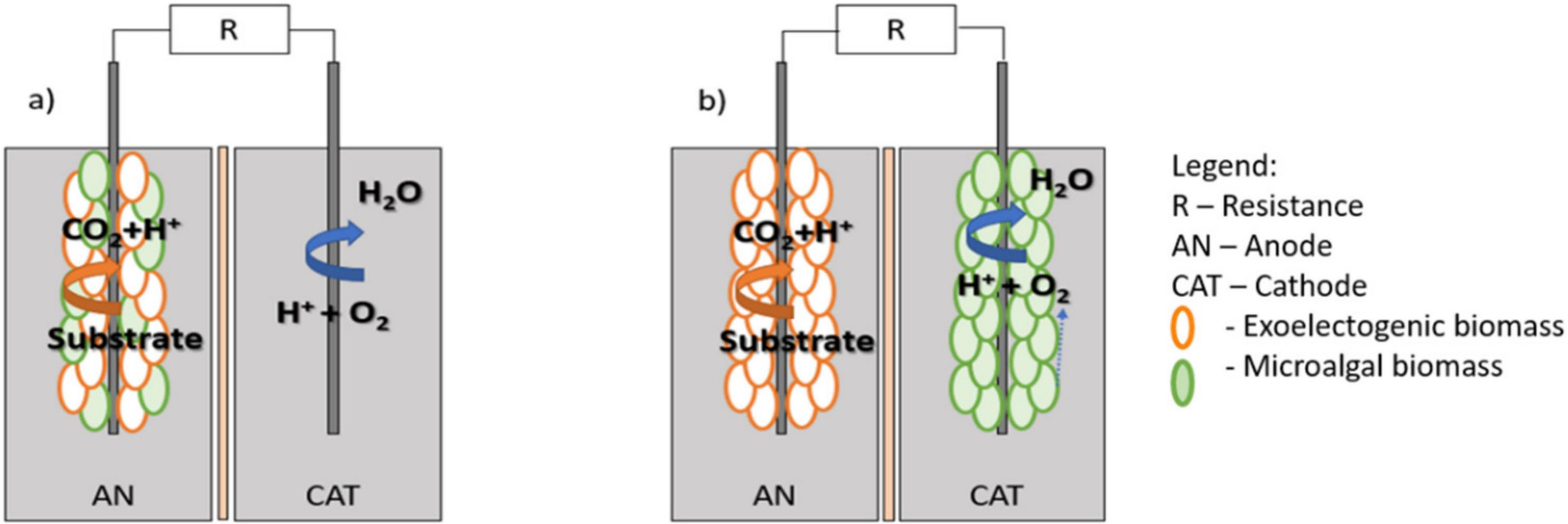
Biochar production from sewage sludge and microalgae mixtures

- nutrient removal by microalgae occurs without costly bio-denitrification processes
- mixed biomass (sludge and microalgae) originates a solid residue after pyrolysis with excellent properties for reuse in agriculture



Hybrid Algae-MFC Systems

- Algae contribute to global CO_2 mitigation processes.
- Combination of algae and MFCs promises to be favourable technological setup.
- Algae function as efficient electron acceptors in cathodic photosynthetic reactions and electron donors at the anode in syntrophic interaction with EABs
- Integration of microalgae in MFC anodic chambers has proven efficient due to their characteristics as substrate, in terms of carbohydrates, lipids, and proteins
- Microalgal biocathodes avoid use of expensive catalysts, such as platinum: mitigate costs
- Algae-MFCs will function with minimal net energy input since need for O_2 supply is avoided, being generated by photosynthesis.



Integrated Photo-Bioelectrochemical (IPB) system

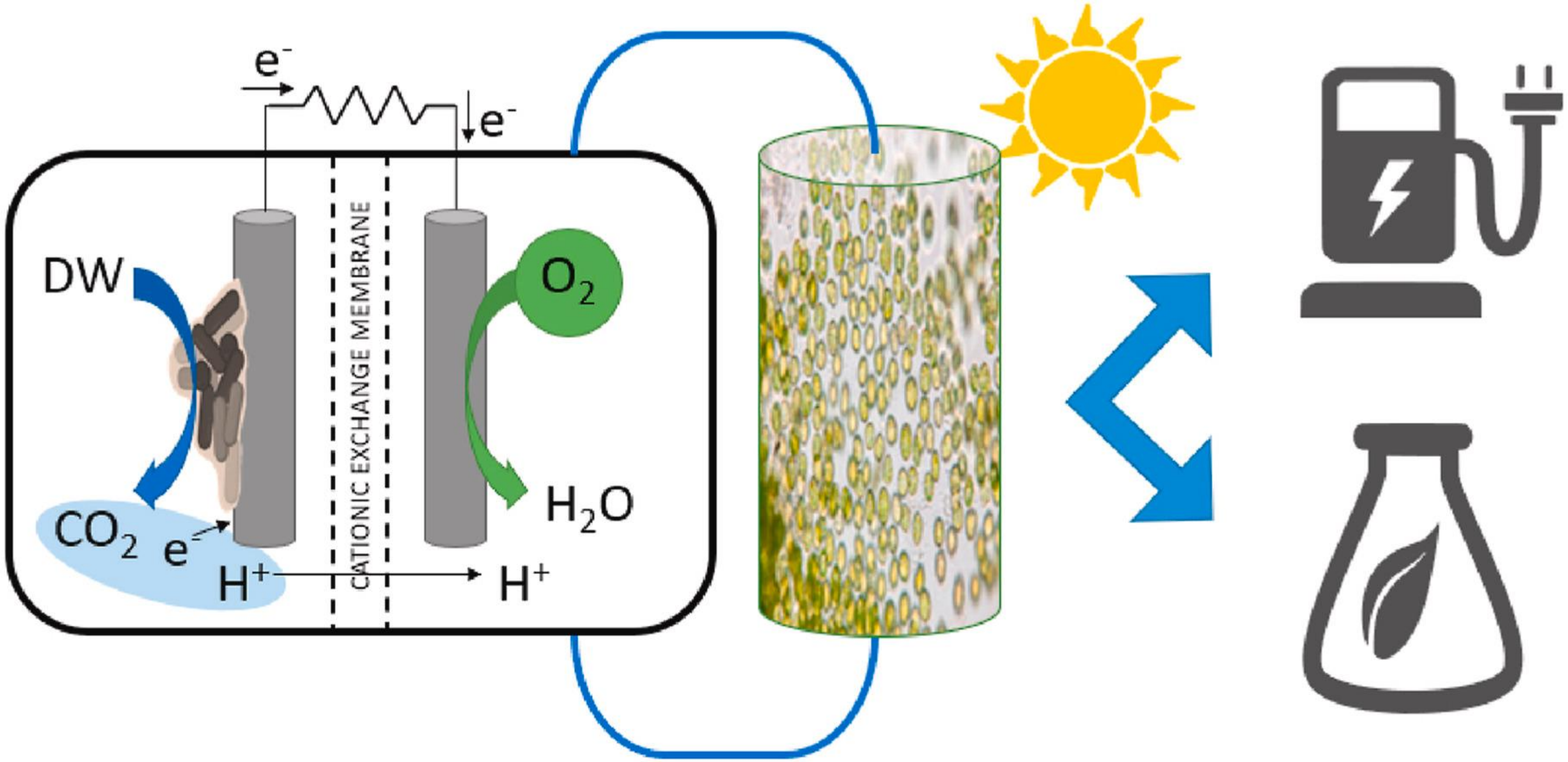
algal biocathode system

Hybrid Algae-MFC Systems

Summary of experiences in hybrid MFC-microalgae integrated systems.

Substrate	Microalgae Species	Configuration	CE (%)	ηCOD (%)	Power Density (W m^{-3})	Ref
Domestic wastewater	*Chlorella vulgaris*	Two chambers	72	5.47	3.1	[**Bazdar et al Bioresour. Technol. 2018**]
Domestic wastewater	*Chlorella vulgaris*	Two chambers	N.A.	44	19	[**Hou et al Bioresour. Technol. 2016]**
Micro-algae	*Chlorella vulgaris*	Two chambers	6.3	90	8.7	[**Cui et al Energy Conv. Manag 2014**
Domestic wastewater	*Chlorella vulgaris*	Two chambers	85	N.A.	5.6	[**Wang et al Biosens. Bioelectr. 2010]**
Acetate	Mixed culture	Two chambers	N.A.	90	8.7	[**Xiao et al Envir. Sci. Technol. 2012**]
Glucose	*Chlorella vulgaris*	Three chambers	N.A.	65.6	0.15	[**Kokabian & Gude Chem. Eng. J. 2015]**
Dairy wastewater	Mixed culture (*Chlorella*)	Two chambers	9	98.1	1.9 ± 0.5	[**Bolognesi et al Environ. Res. 2021**]

Combined microalgal photobioreactor/MFC



Algae-derived fuels (3rd generation biofuels)

- Algae and microalgae can produce energy directly by extraction of lipids, or indirectly as feedstock for fermentation processes
- Algae produce oil easily refined into diesel or even gasoline components
- Fermentative bacteria can degrade algal biomass for biobutanol production
- Algae can be genetically manipulated to produce a number of biofuels: biodiesel, biobutanol, biomethane, bioethanol, vegetable oil, and even jet fuel
- Capable of much higher and advantageous yields than other feedstocks
- Algae-growing facilities can be tied to carbon-emitting point sources (power plants, industries, etc.) to convert gaseous emissions into fuel directly, reducing total emissions by avoiding the carbon cost of nitrification and denitrification

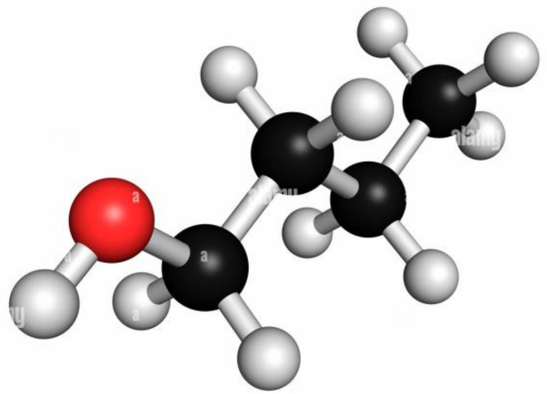
Algae-derived fuels (3rd generation biofuels)

- algae are potentially easier to cultivate than any other traditional biofuel crop
- algae can be grown almost anywhere (if ambient temperatures warm enough)
- no farmland needs conversion
- algal technology only major downside: amounts of water and nutrients (N & P) to grow
- algae can be grown in wastewater, performing tertiary municipal sewage treatment without taking up additional land
- to generate 1 kg of biodiesel from microalgae 0.33 kg N, 0.71 kg P, 3726 kg H_2O are necessary: use of wastewater reduces by 90% the need for water, completely fulfils nutrient demand

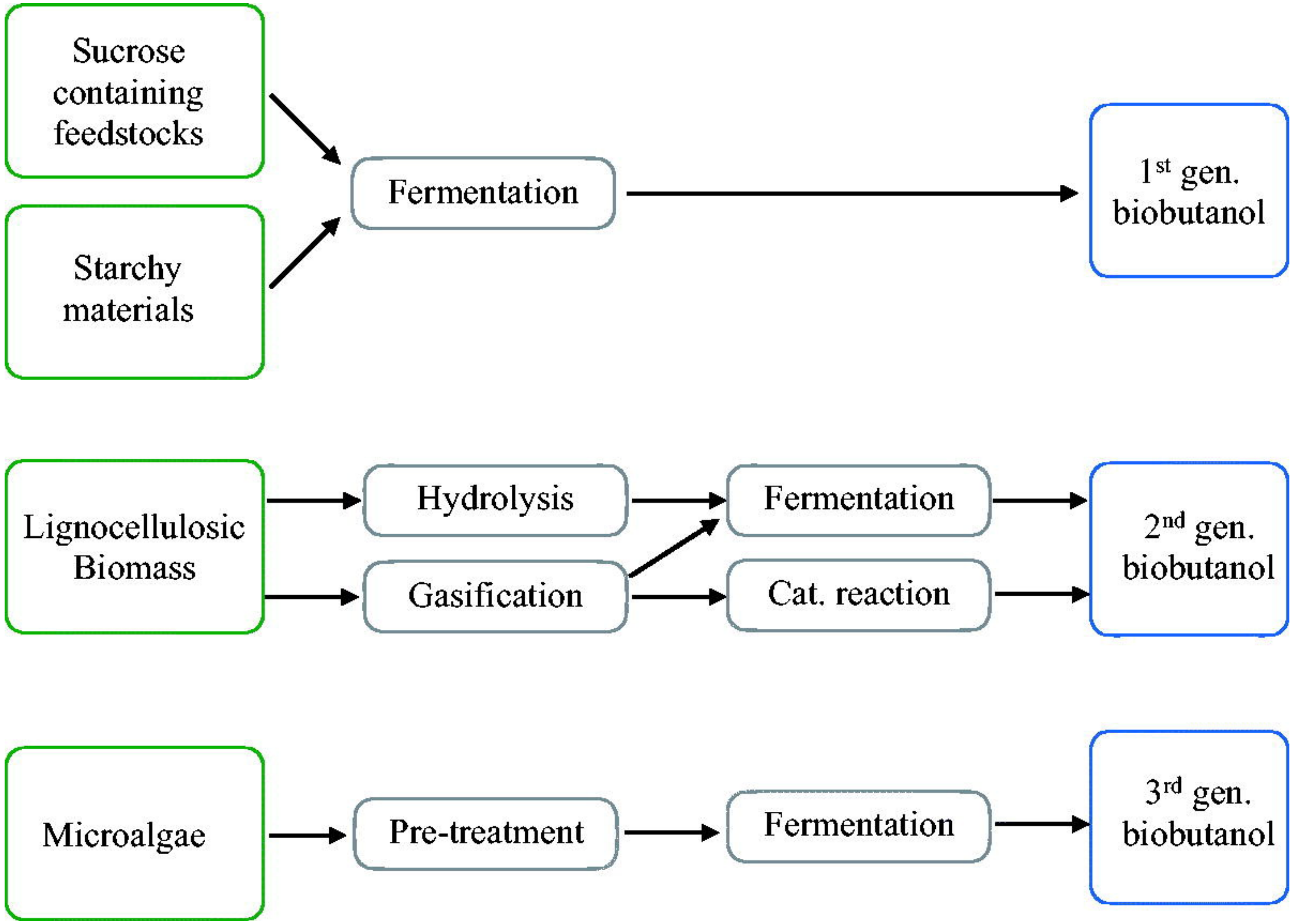
Biobutanol production from microalgae

- Butanol: renewable fuel with great benefits when used in internal combustion engines, still less known than ethanol and biodiesel
- produced by fermentation of biomass, easily blended into gasoline, miscible with diesel (to reduce emissions), contains more O_2 than biodiesel
- Biobutanol may reduce NO_x formation during combustion, due to higher evaporation heat (reduces internal engine temperature)
- microalgae considered very promising for biobutanol generation due to high growth rates and carbohydrate content.

$CH_3(CH_2)_3OH$



Biobutanol production from microalgae



Biobutanol production from microalgae

- Harvested algal biomass pretreated to release monosaccharides (microalgal sugars), and fermented.

- *Clostridium acetobutylicum* converts residual solid matter in the liquor to butanol

- butanol yield higher when unfiltered hydrolysate is processed: yield 21.96 mg biobutanol/$g_{residues}$ vs 10.03 mg/$g_{residues}$ of filtered one

Microalgae biorefinery

- High-value co-products extracted from algae biorefineries:

pigments, proteins, lipids, carbohydrates, vitamins and anti-oxidants (applications in cosmetics, nutritional and pharmaceuticals industries)

- Innovative microalgae biorefinery schemes can apply supercritical fluid extraction methods for higher yields and ease of operation
- feasibility of multi-product cogeneration led to efficient production pathways and enhanced recovery of materials and energy
- improvement must still be achieved on economics of algal biofuel production for market competitiveness with fossil fuels.
- some conversion processes are complex and expensive, but could turn commercially viable by optimization and exploitation of all by-products

Microalgae biorefinery

- Microalgae used as feedstock suitable to biohydrogen fermentation

- Some algal species (*Chlamydomonas reinhardtii, Chloroccum sp., Dunaliella tertiolecta, Nitzchia closteriu, Phaeodactylum tnicornutum, Spirulina platensis*) have high photosynthetic efficiency and capability of carbohydrate accumulation (up to half their dry weight)

- Future of algal biofuels based on developing cost-effective approaches for the most operationally efficient technologies

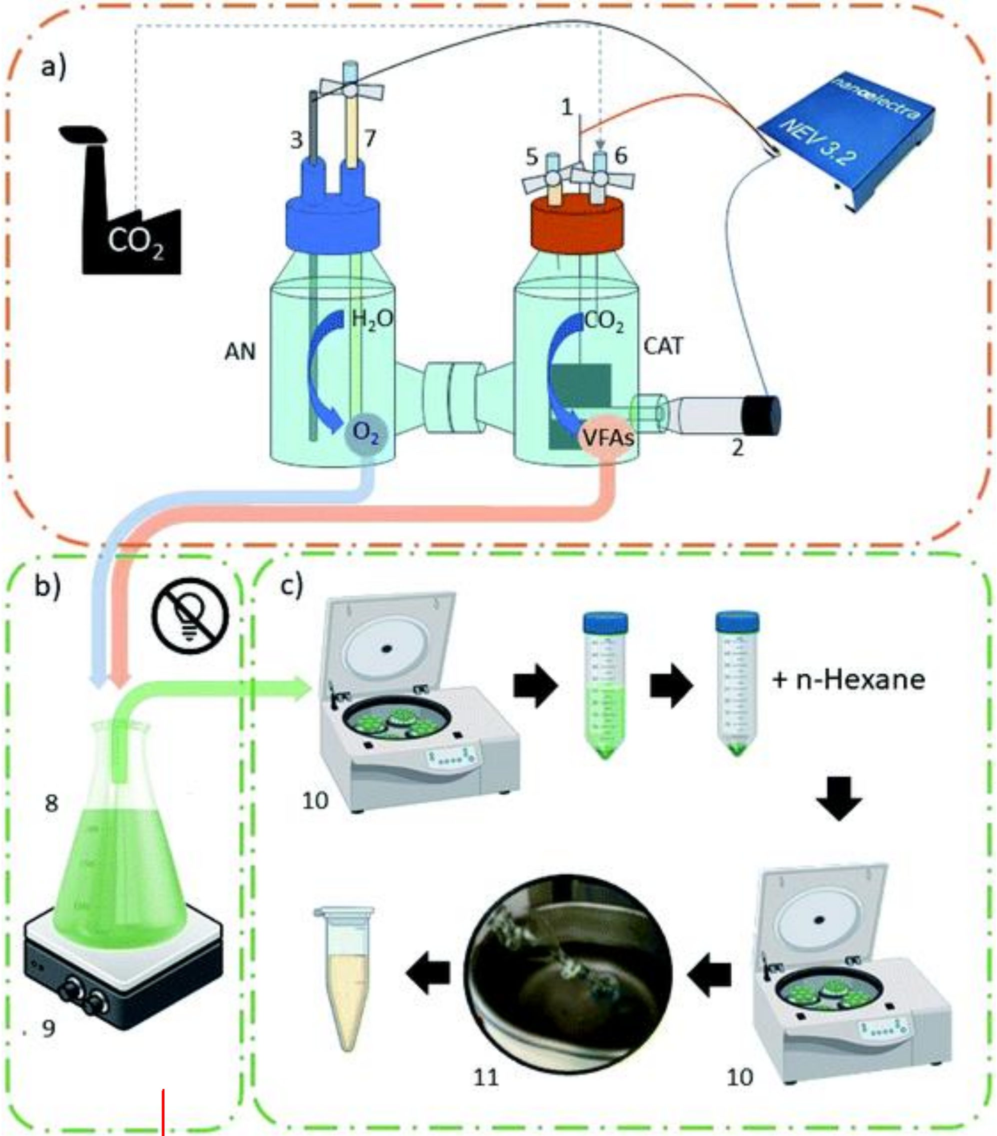
CO_2 to bio-oil in bioelectrochemical system-assisted microalgae biorefinery

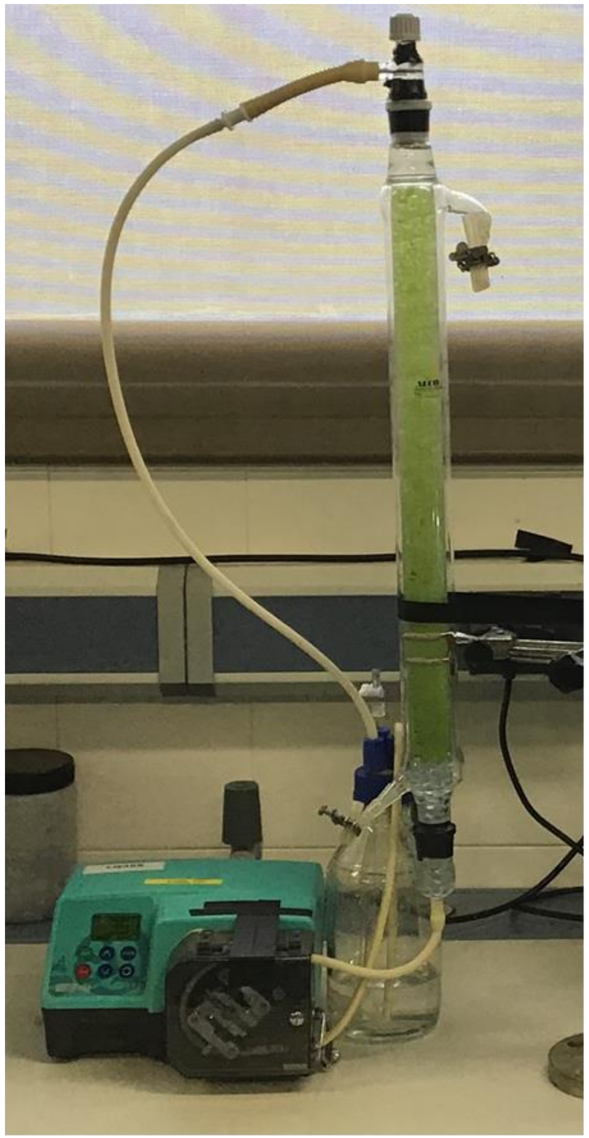
- Microbial electrosynthesis (MES) for bioelectro CO_2 recycling is a sustainable opportunity to exploit off-gases from industrial facilities, convert them into energy
- two-step process based on coupling BES and heterotrophic *Auxenochlorella protothecoidesis* converts CO_2 into biodiesel compatible oil
- Biodiesel produced from microalgal oil presents high heating value (41 MJ/ kg) and H/C ratio (1.81), fully compatible with ASTM biodiesel standards
- microalgae are grown using VFAs produced in biocathodes (WWTP effluents used as substrate) with CO_2 as the sole carbon source
- oil yield of up to 22% w/w was assessed: 0.03 kg bio-oil per kg CO_2 captured can be recovered.

CO_2 to bio-oil in bioelectrochemical system-assisted microalgae biorefinery

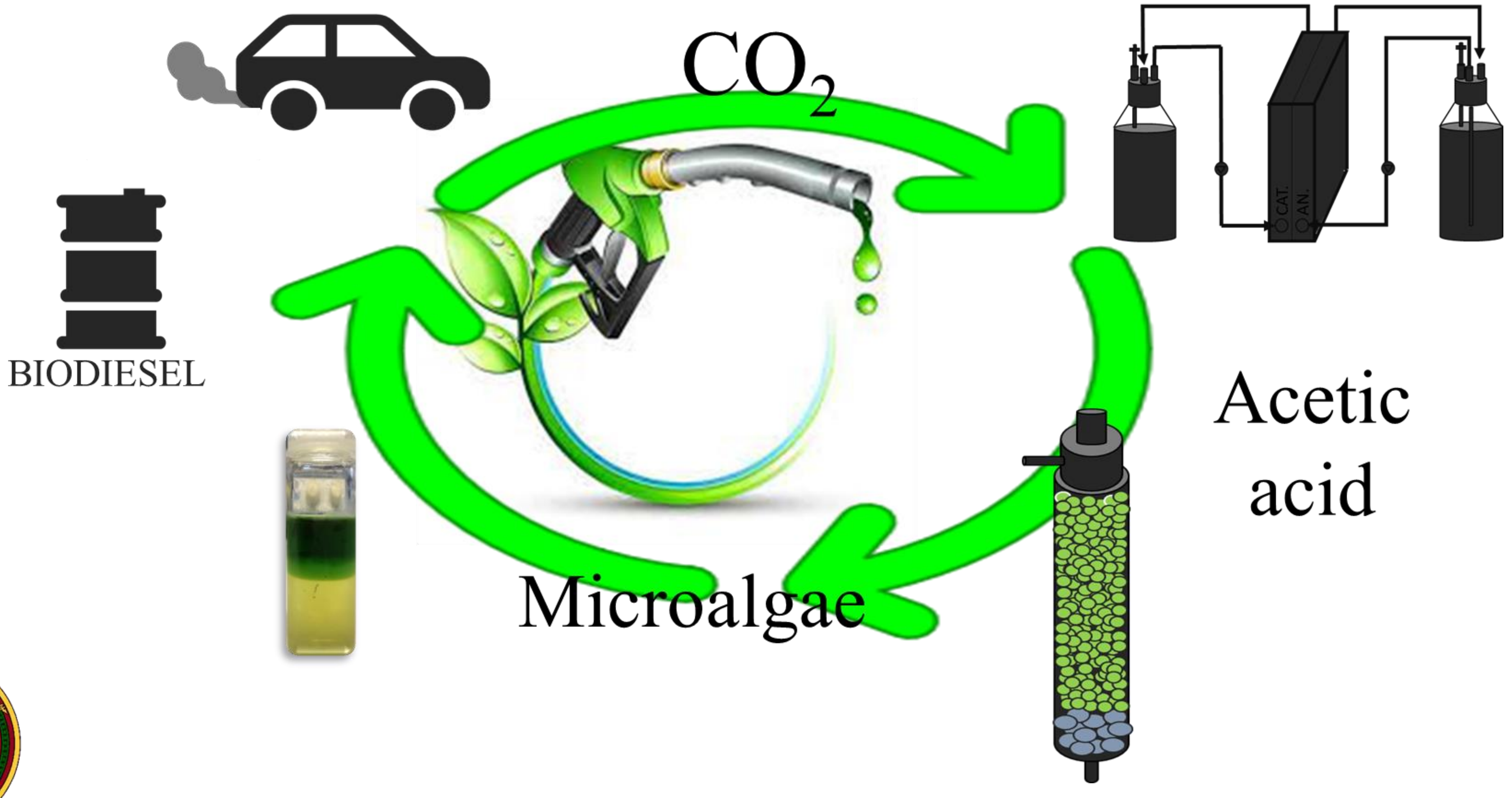
Microalgae exploit carbon compounds produced at the biocathode of MES reactor and O_2 produced from water splitting at the anode.

Oil extraction is achieved by evaporation after cell disruption and centrifugation.





CO_2 to bio-oil in bioelectrochemical system-assisted microalgae biorefinery



Thank you, and ……

One at a time, please!!!