TURNING CO_2 INTO VALUE

FUELS & CHEMICALS FROM SOLAR ENERGY | THE PHOTO2FUEL JOURNEY

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NEFERTITI
Innovative photocatalysts integrated in flow photoreactor systems for direct CO_2 and H_2O conversion into solar fuels

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LEITAT
managing technologies

Introduction

It is projected that by the end of years 2025, the energy requirement would be ~15,000 Mtoe (million tones of oil equivalent), and by 2040 will grow to ~18,000 Mtoe.

This means an estimated emission in 2023 of 37.4 giga tones of CO_2 equivalents. August 3rd, the average CO_2 concentration in air in the planet was 425.76 ppm.

28 % of fuel consumption and 23% of CO_2 emissions due to transport.

CALVIN, Katherine, et al. IPCC, 2023: Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, H. Lee and J. Romero (eds.)]. IPCC, Geneva, Switzerland. 2023.

This project has received funding from the European Union’s Horizon 2021 research and innovation programme under grant agreement No 101022202.
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NEFERTITI

Introduction

Renewable fuels (aka sustainable fuels or neutral emission fuels)

Zero-carbon fuels

e.g. hydrogen and ammonia.

Sustainable when produced using energy from sustainable resources

Biofuels

e.g. bioethanol, FAME, biomethanol

Derived from biomass.

In the last years EC has changed policies and no longer consider biofuels as “sustainable”

Synthetic fuels (aka e-fuels)

e.g. methanol, diesel, methane,…

From CO_2 and H_2 (or water)

Sustainable when produced using energy from sustainable resources (green hydrogen)

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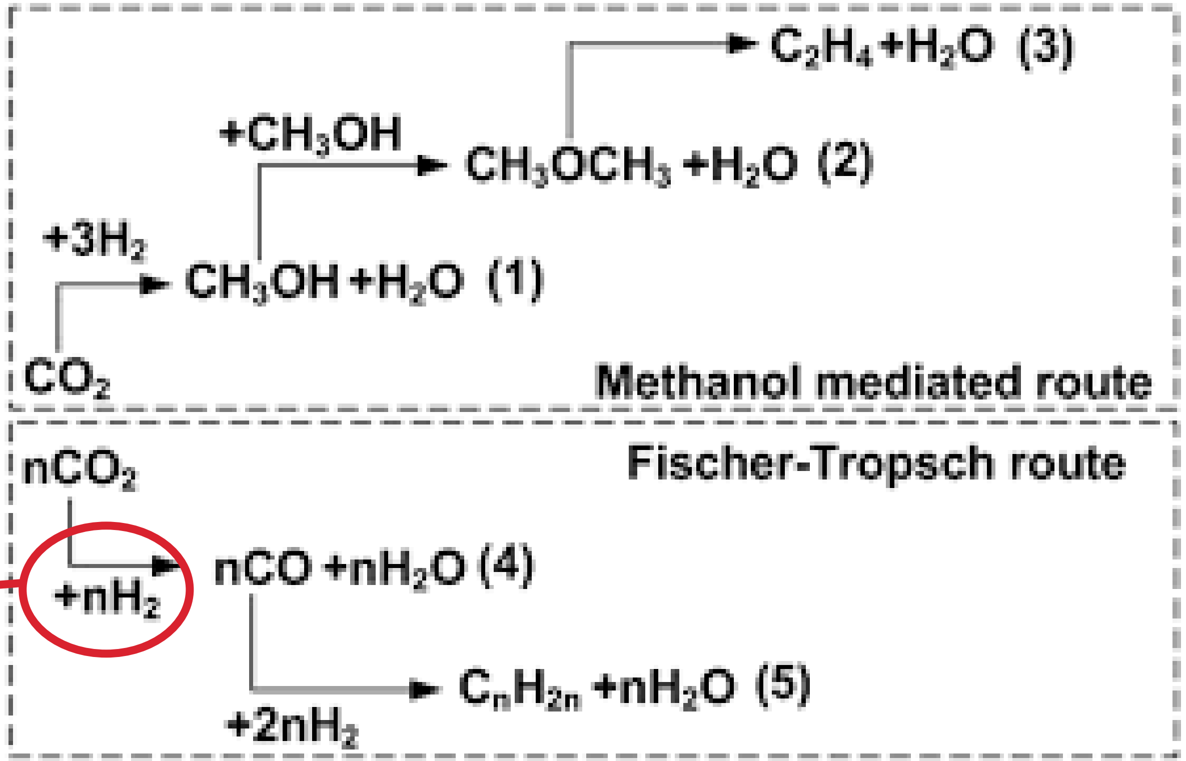
Introduction

Synthetic fuels (e-fuels)



Water splitting (*in situ*)

Electrolysis, **photocatalysis** or termal catalysis

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Introduction

Synthetic fuels (e-fuels)

Advantages of Photocatalysis

1.Energy savings: Unlike electrolysis, photocatalysis directly uses sunlight, which could reduce electricity consumption (typically the highest cost in electrolysis).

2.Process simplicity: Photocatalysis can be more straightforward since it uses light and a photocatalyst to break water molecules or convert CO_2.

3.Less infrastructure: With the development of efficient materials, photocatalytic reactors could be cheaper and less complex than electrolyzers.

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Synthetic fuels (e-fuels)

Challenges of Photocatalysis

1.Low efficiency: Currently, the energy conversion efficiency is much lower than electrolysis.

2.Material stability: Many photocatalysts degrade over time or under prolonged exposure to light.

3.Scalability: Electrolysis is already quite advanced and easier to scale, whereas photocatalysis is still in the experimental stage.

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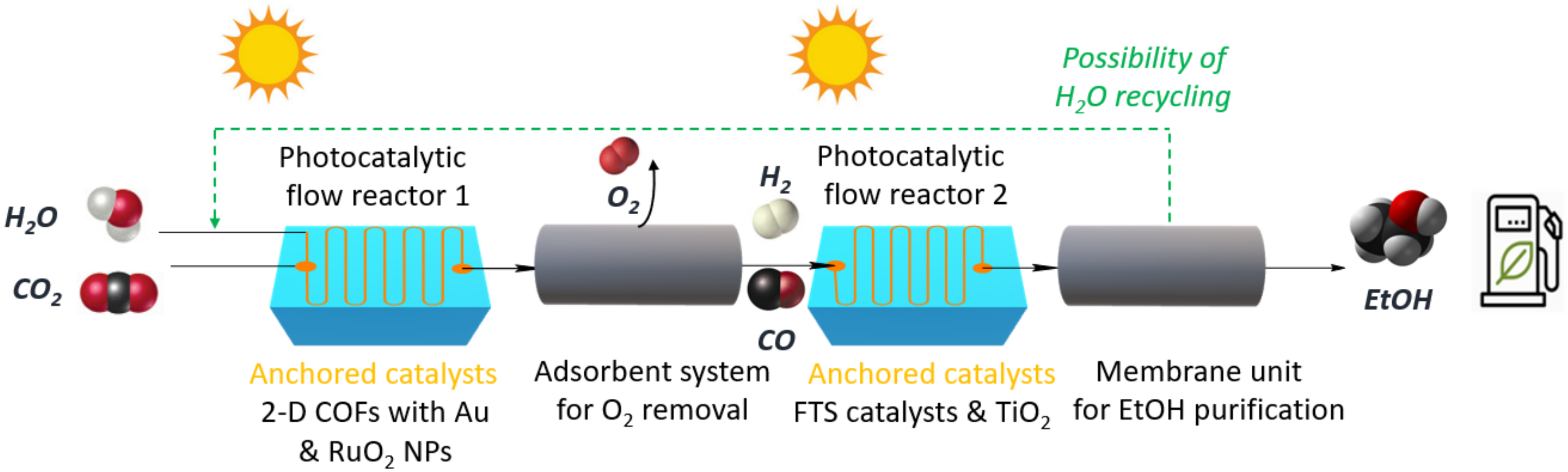
Objectives

To develop an efficient photocatalytic (PC) process in a single device for the synthesis of fuels from CO_2 and H_2O as alternative to multistep processes involving fossil fuels

Novel and challenging approach-> two connected flow reactors to perform two reactions

- **1st reactor**->Use of enhanced heterogeneous photocatalysts to perform the simultaneous conversion of CO_2 and H_2O, by mimicking Z-scheme photocatalysis found in nature, to produce syngas.
- **2nd reactor**->Use of enhanced heterogeneous photocatalysts to transform the syngas into ethanol and C_{2+} alcohols.



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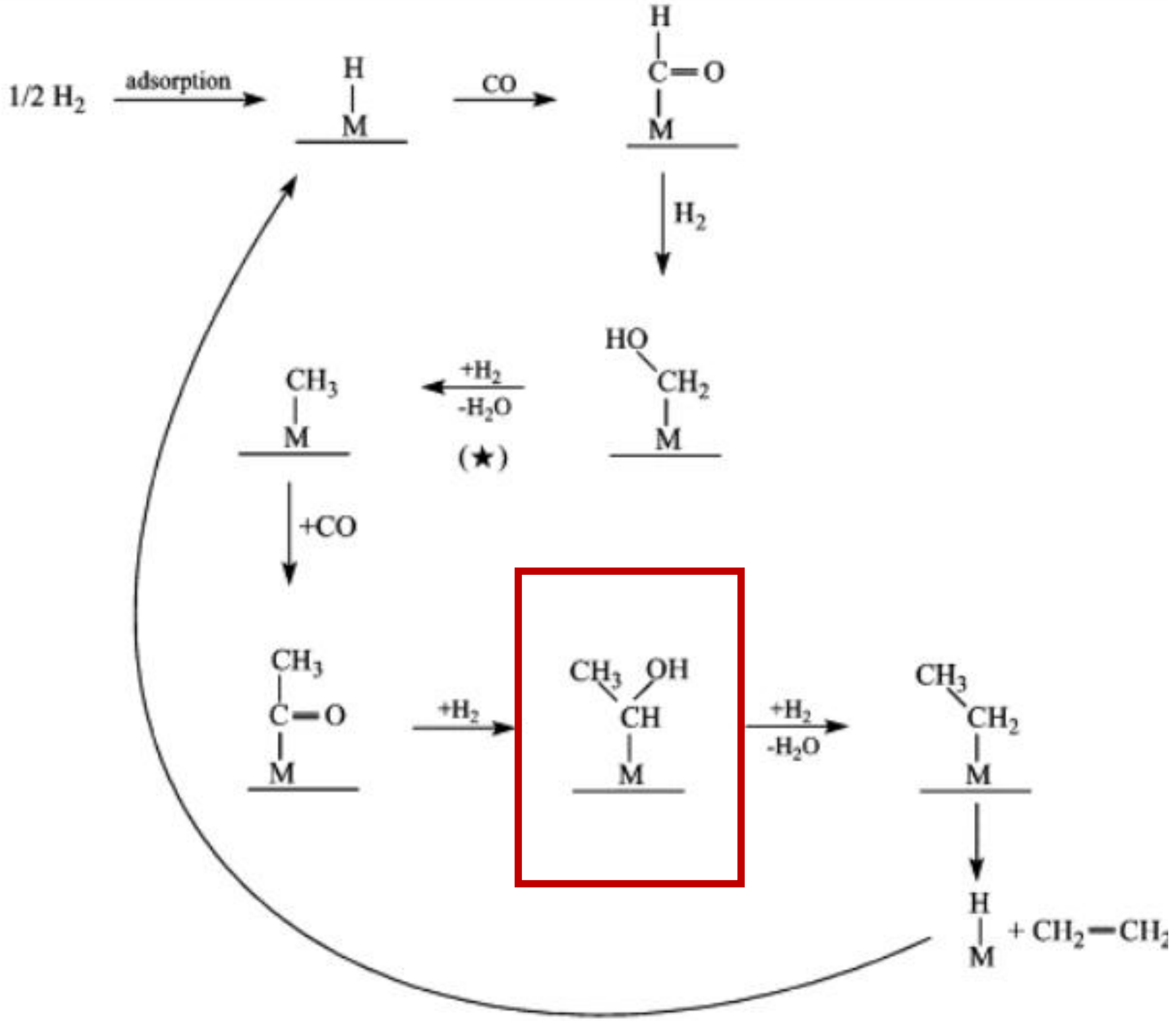

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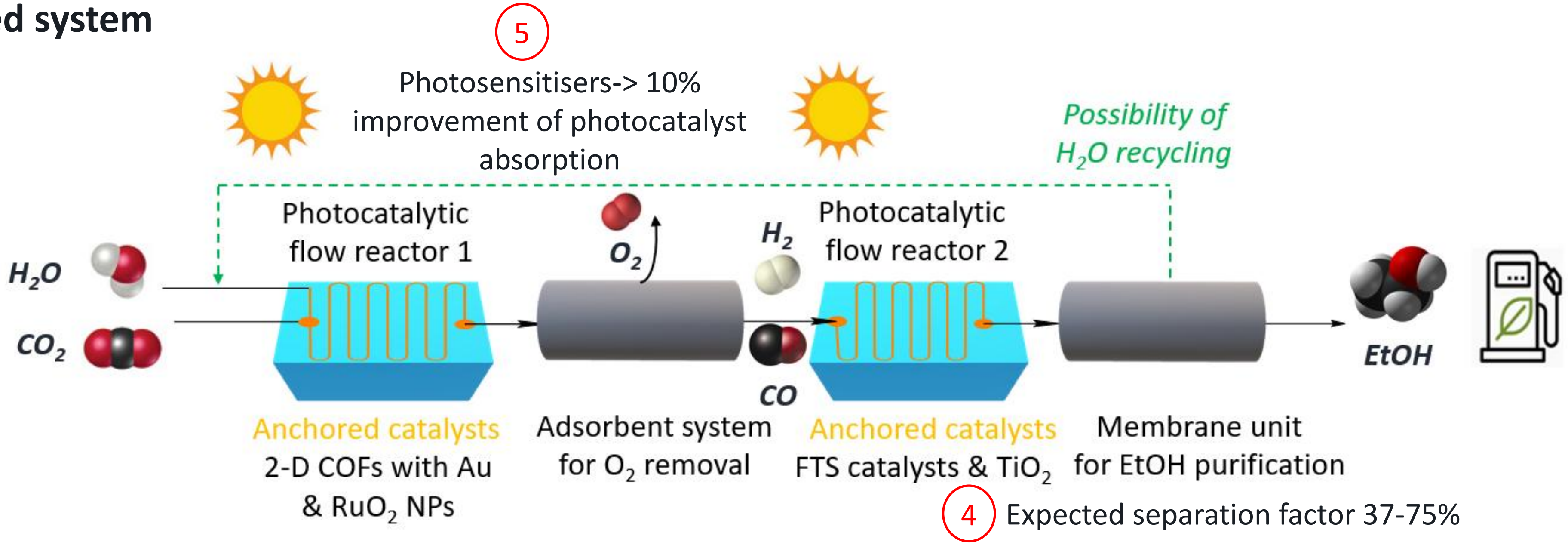
KPI

Integrated system



(1)
- -STCO up to 5%
- -Selectivity up to 99%
- -Stability < 5% over 100h

(2)
- -Selectivity 40-50% for C_{2+} alcohols
- -Conversion up to 70%
- -Stability < 20% over 200h

(3)
- -STF efficiency 3-5%
- -Selectivity up to 50% (ethanol)
- -Performance < 5% over 1-5 days

(6)
- -Process 3-10 mL/min
- -Validation indoor under 1 sun illumination for 1-5 days
- -Validation outdoor under sunlight for 5h

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Consortium

- 10 Partners
- 7 Countries (4 European and 1 Associate country)
- 2 International partners (China and the USA)

Value Chain

Photocatalysts design for CO_2/H_2O	Photocatalysts design for C-C bond	Photosensitizers and optical design	Flow reactors design and manufacture	Photocatalysts and photosensitizers deposition	Flow reactors testing and process modelling	Validation of integrated evice, techno-economic validation and LCA/LCC
NUI Galway OÉ Gaillimh	Peking University	ICIQ, LEITAT Technological Center	CHEMTRIX	FUNDITEC, LEITAT Technological Center	LEITAT Technological Center, University of Michigan	SOCAR, Universidad de Burgos, Stratagem Research · Innovation

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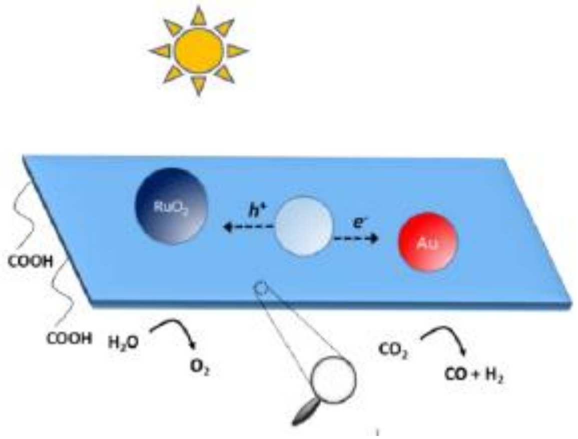
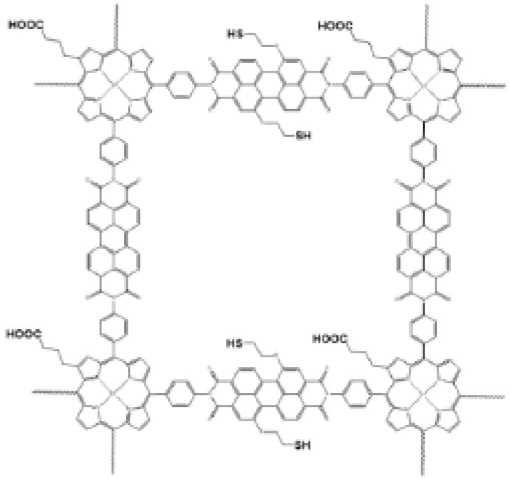
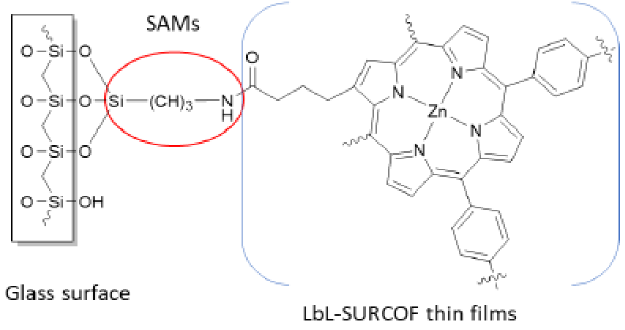
Methodology

Photocatalysts for the simultaneous CO_2 reduction and H_2O oxidation

- Optimization of photocatalysts will be predicted by computational methods to enhance their performance
- 2-D COFs will be used as semiconductors and will be modified with functional groups to be anchored to the inner part of the reactor
- 2-D COFs will be doped with Au NPs, for the reduction of CO_2 to CO, and RuO_2 NPs, for the oxidation of H_2O to O_2 and H_2







- Microchannel's surface will be activated with piranha sol. to have OH groups which will react with APTEs to give a NH_2 groups on the surface (Self Assembly Monolayers, SAMs)
- Surface-mounted COFs (SURCOFs) will be synthesized by covalent anchoring 2-D COFs to a SAMs, through amide bond, situated on the inner walls of the glass reactor

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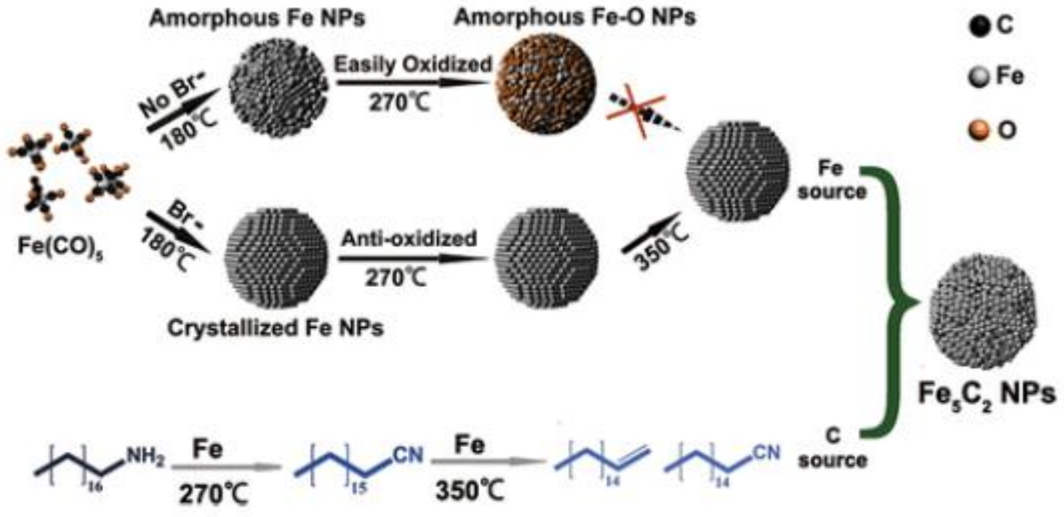
Methodology

Photocatalysts for CO reduction and C-C bond formation into solar fuel

- Optimization of photocatalysts will be predicted by computational methods to enhance their performance
- FTS catalysts (not including PG-based materials) like Fe_5C_2 NPs together with metal oxides (TiO_2 or Fe_xO_y) and doping agents will be used to transform syngas (mixture of CO and H2) to fuels (alcohols and C_{2+} alcohols)



- The catalysts will be anchored to the inner part of the reactor by treatment of glass surface with piranha sol. and subsequent sol-gel treatment

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Methodology

Light-harvesting systems

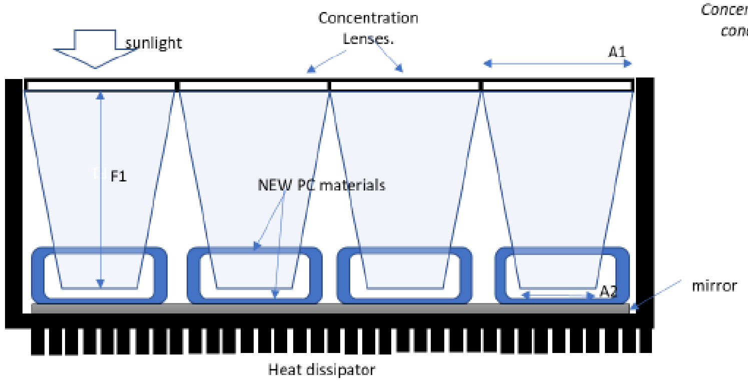
Luminescent Solar Concentrator (LSC)

- Use of dyes like rhodamines or perylene(bisimides) derivatives to increase the photon absorption by the photocatalysts and the efficiency of the process
- Persistent luminescence materials (ZrO among others) will be also tested. Such materials provide continuous light irradiation (hours) upon exposure to UV light for seconds
- LSC will be deposited at the external part of the reactor by spin-coating and spray-coating techniques using polymers

Optical device

- Lenses, beam-splitter and mirrors will be used for optimal sunlight profit

Fresnel lenses based Concentrator concept



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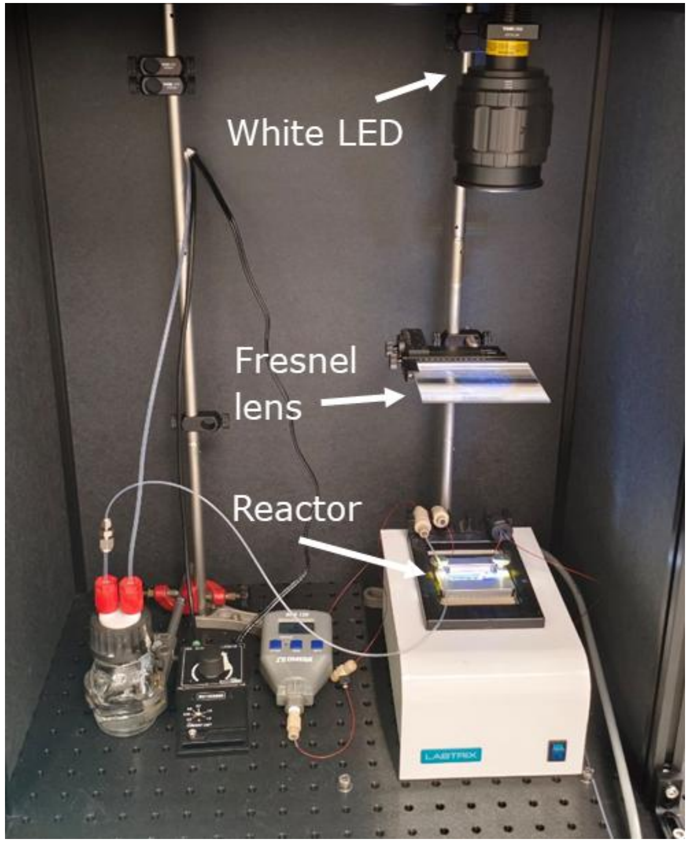
Methodology

- Adapting reaction time to flowrate adjusting retention time.
- Adapting retention time to flow kinetics. Heat and mass transfer. Higher contact with light source.
- Catalyst anchoring and influence in flowrate stability and over pressure.
- Stabilizing time. Long time until all the parameters ready (T, P, flowrate…).



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Methodology

- Inline analysis vs collected analysis.
- Changing parameters between measurements is not suitable. Stablish catalyst activity on batch experiments.
- Each calibration for inline analysis is only valid for specific parameters (flowrate, T, P).

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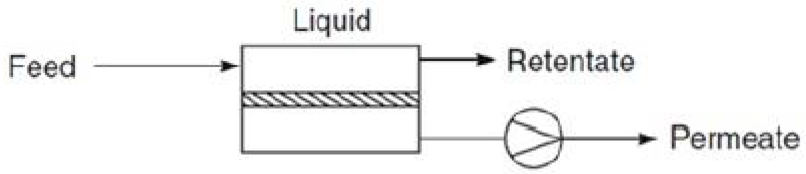
Methodology

Ethanol membrane separation and purification

- Use of pervaporation (PV) process to purify ethanol of the mixture from the second reactor
- Use of organophilic membrane (hydrophobic polymer) for ethanol purification
- Incorporation of nanoparticles (zeolites or silica) into the polymer membranes will increase separation rate
- Other C_{2+} alcohols formed during the process will be also separated



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Results at the moment

CO_2 + H_2O to syngas

- Catalysts with AU-NPs and RuO2 over COF and Carbon Nitride prepared.
- CO and H_2 obtention demonstrated under 1 sun.
- At temperatures over 150 °C, overreduction to methane.

Syngas to C2+ alcohols

- Catalysts with hMnLiFe/ND@G and RhMnLiFe/CNT prepared.
- >50% selectivity towards C2+ alcohol at very low conversion.

Purification systems

- Inorganic membrane selectively separates O_2 from syngas.
- Hydrophobic membranes with >80% selectivity in ethanol purification.

System scale-up for December

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