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MODEL-BASED SCREENING OF ELECTROCHEMICAL REACTION PATHWAYS FOR THE INTEGRATED BIOFUELS SYNTHSIS AND CO_2 REDUCTION

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E-Bio-Fuel: Electrosynthsis of biofuels via co-valorisation of bio-fermentation products and captured CO_2—A feasibility study

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Supergen Bioenergy

Department for Transport

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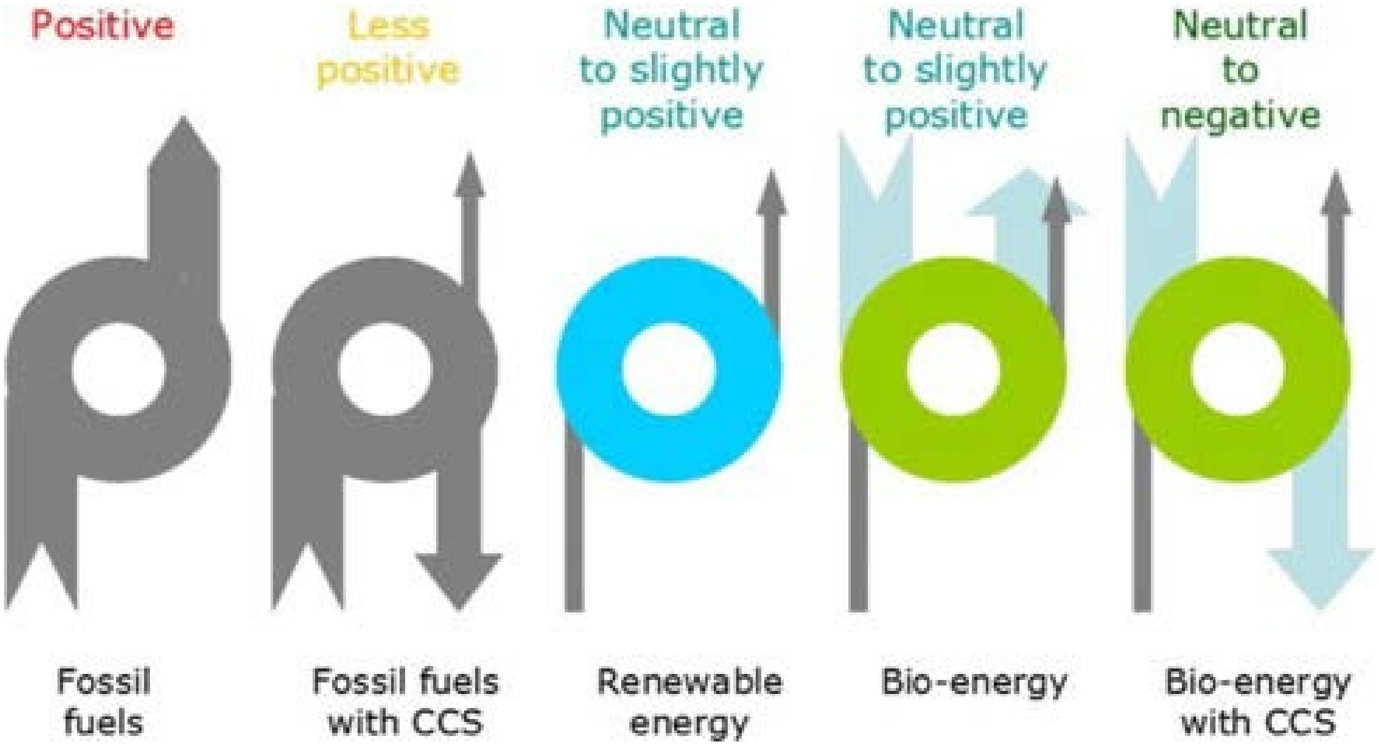
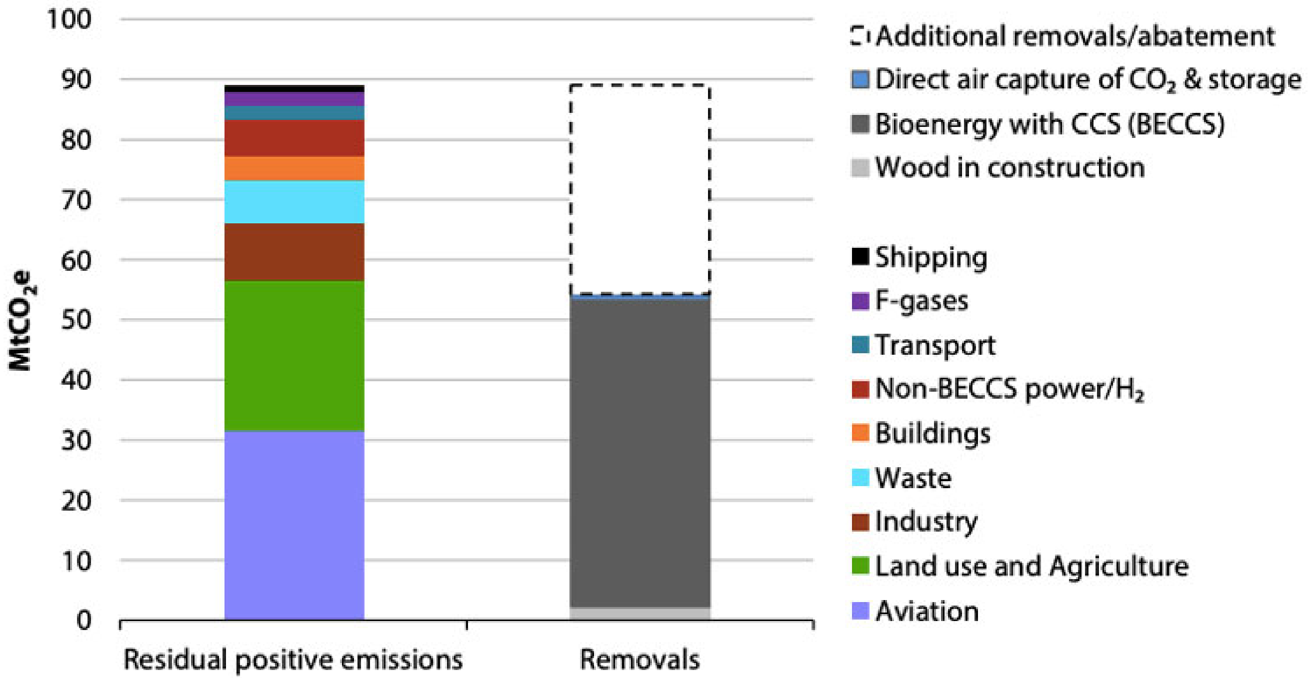
BECCUS-bioenergy with CCUS



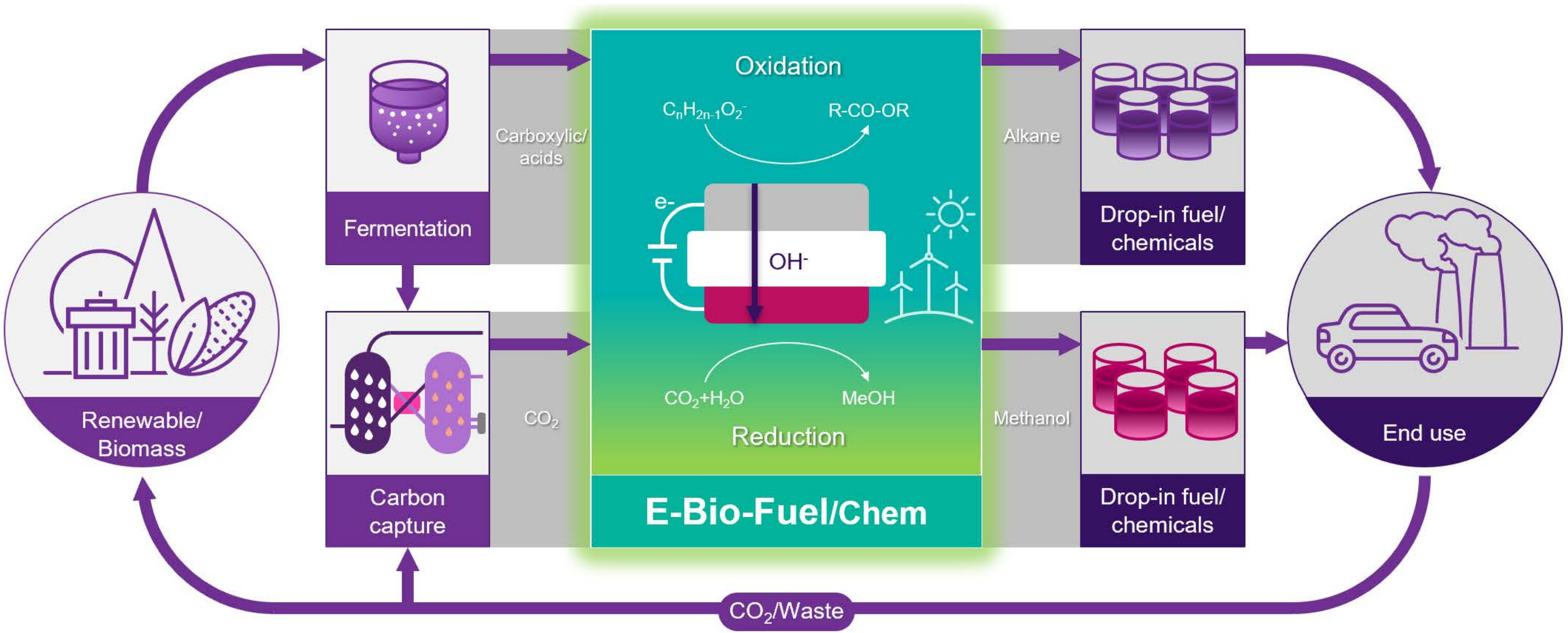
Negative emission technologies



Biofuel with CCS to play a key role in UK's emission removals & offsets

Our vision

E-Bio-Fuel Circular Economy



The idea behind

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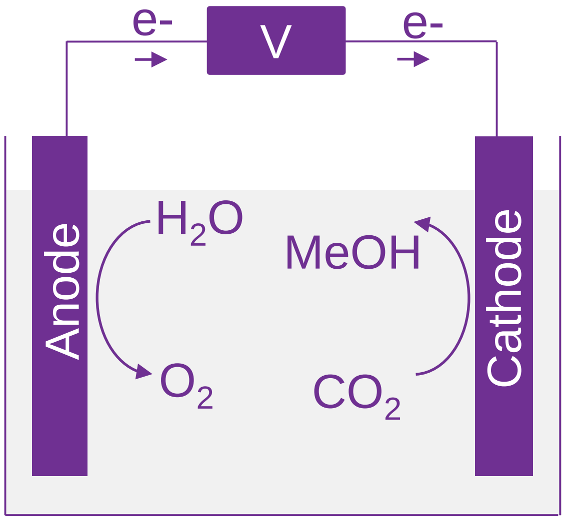
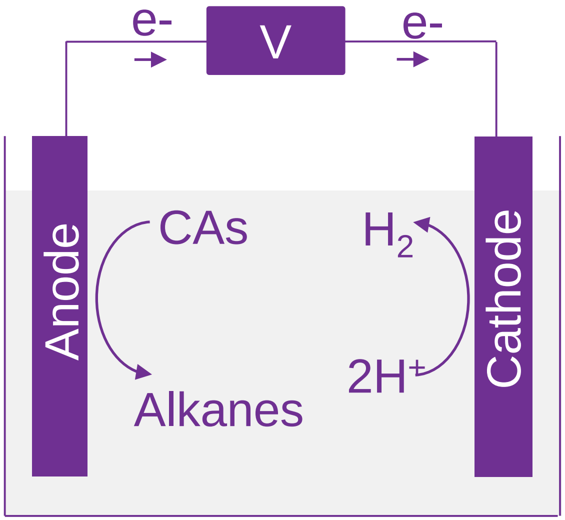
CO_2 valorisation:

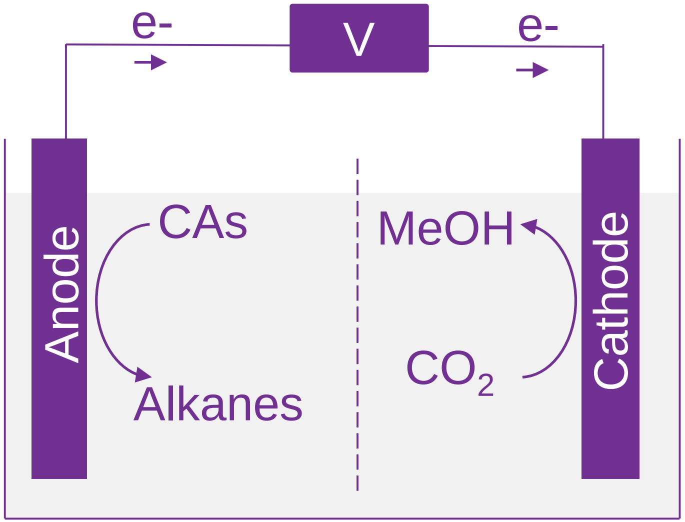


Biomass valorisation:



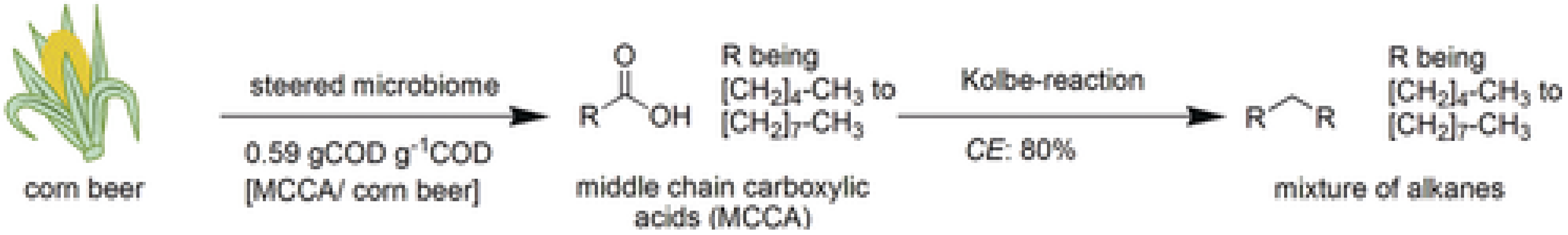
Kolbe electrolysis

Redesign the system



The proposed bifunctional system

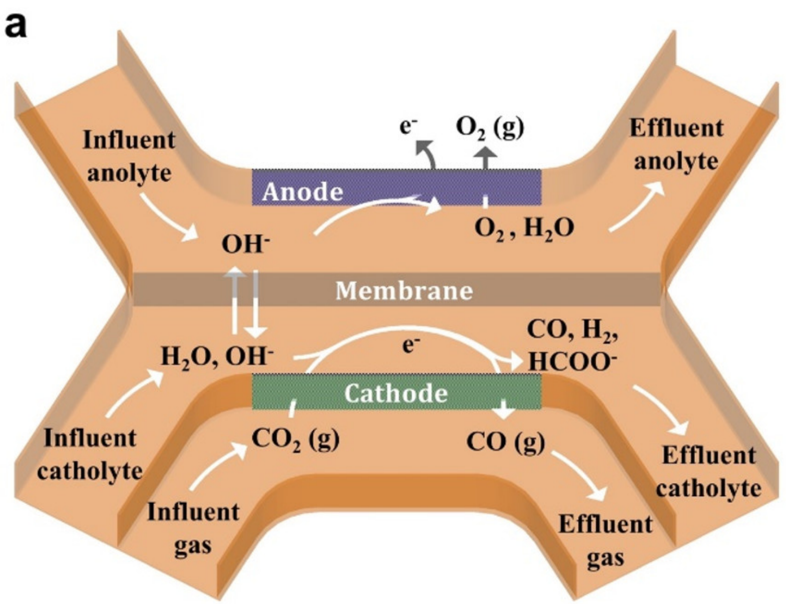
The chemistry (1)

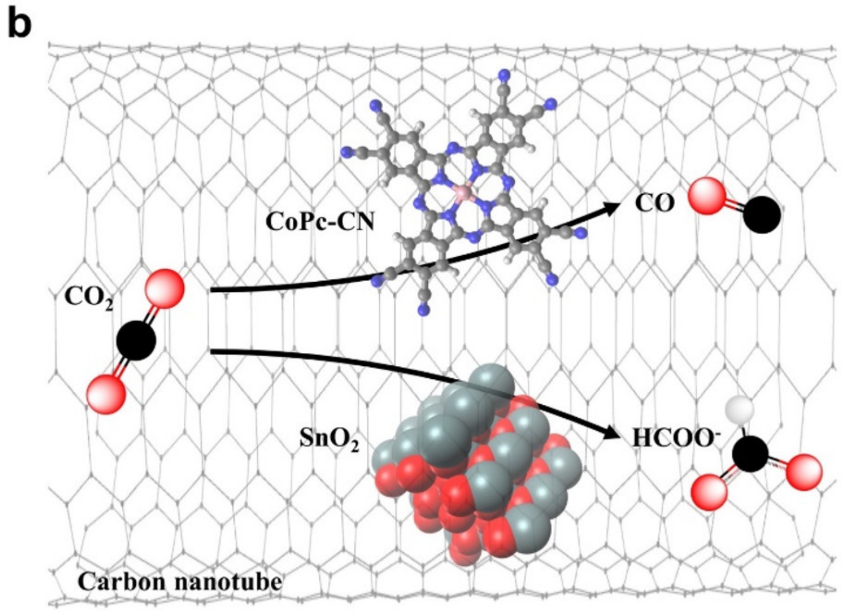


Electrobiorefineries: Unlocking the Synergy of Electrochemical and Microbial Conversions, Angewandte Chemie International 2018, 57,10016-10023.

The chemistry (2)

High performance electrochemical CO_2 reduction cells based on non-noble metal catalysts





ACS Energy Letters, 2018, 3, 2527–2532 (Most read article)

Background

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Our vision: E-Bio-Fuel Circular Economy

- The project aim is to develop a new paradigm for value-added low-carbon transport fuel production through **multifunctional electrosynthesis for integrated, co-valorisation of biomass fermentation products and the captured CO_2**.

- The novelty of the project lies in the proposed electrosynthesis unit, as an enabler to the synergetic integration of anodic **carboxylic acid (CA) upgradation (to energy dense liquid alkanes biofuel)** with the cathodic **CO_2 valorisation (to produce methanol as drop-in fuel)** to maximise emission reduction, energy use and added value.

- The ultimate goal is to intensively reduce emissions and increase the sustainability of the road transport sector, whilst enhancing renewable energy security.

Methodology

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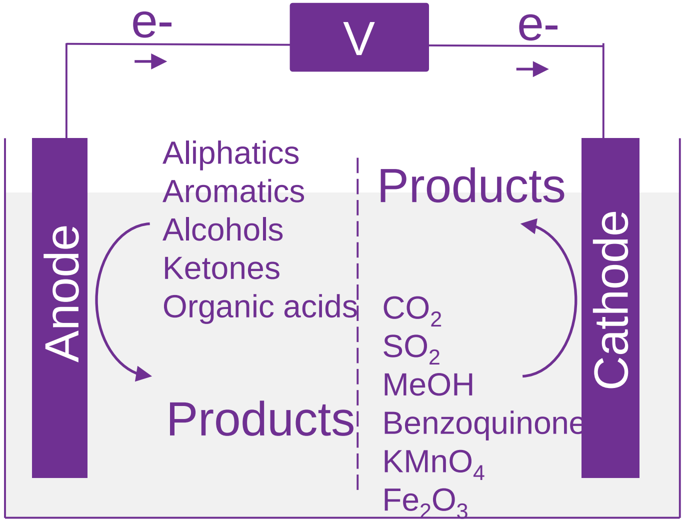
Electrochemistry and experiment:

- Basic electrochemical characterisation are carried out in a batch reactor (IKA ElectraSync 2.0). Main products are then detected by Gas Chromatography Mass Spectrometry (GCMS).

- Initial results show a promising concentration of the desired compounds.



The proposed bifunctional system

MICRA COMMERCIALISATION OF RESEARCH ACCELERATOR

We are engaging with MICRA to commercialise our new technology

MIDLANDS INNOVATION

Aston University BIRMINGHAM UK | UNIVERSITY OF BIRMINGHAM | Cranfield University | Keele UNIVERSITY | UNIVERSITY OF LEICESTER | Loughborough University | University of Nottingham UK | CHINA | MALAYSIA | WARWICK

Methodology

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Computational model assumptions:

- Laminar flow
- Inlet CO_2 at 20 C and 1 atm
- Produced gases dissolve completely in the liquid (bubble mechanics neglected)
- Electrochemical reactions occur at the electrode surfaces

At the cathode:

$CO_2(aq) + H_2O + 2e^- \rightarrow HCOO^- + OH^-$

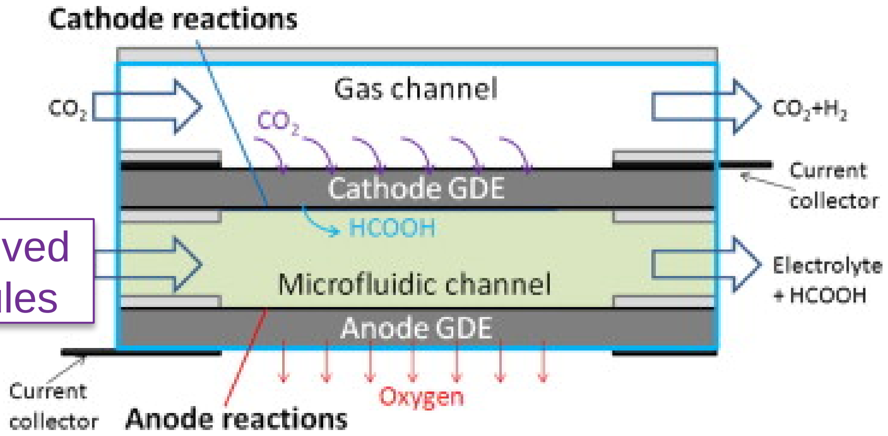
Side reaction at the cathode:

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

At the anode:

$2OH^- \rightarrow 0.5O_2 + H_2O + 2e^-$

Bio-derived molecules



Model schematic

Methodology

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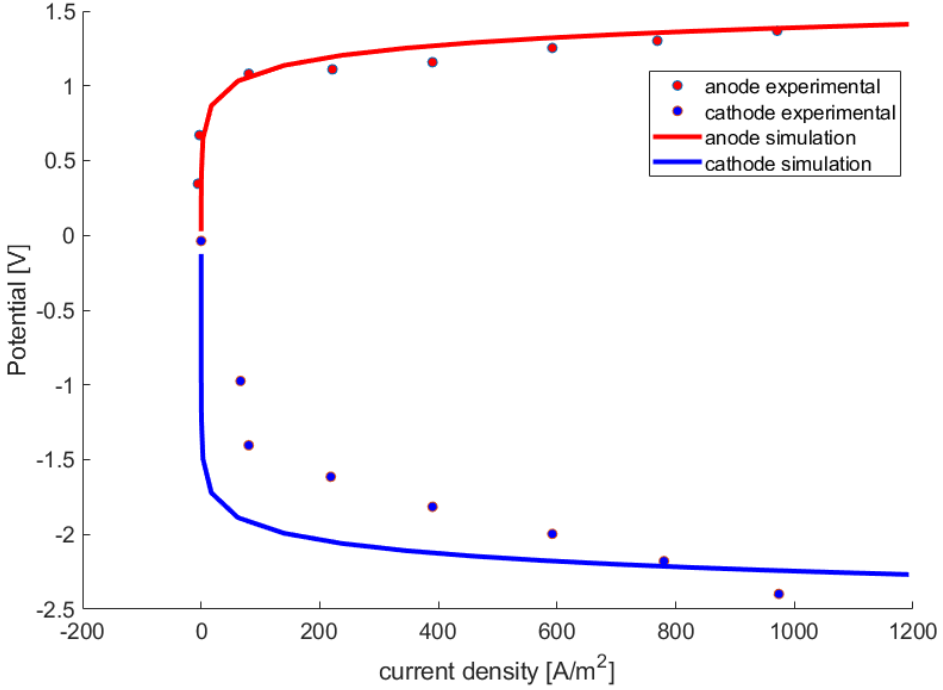
Computational model validation:

- The model was validated by comparing current density vs applied voltage with experiments [1].



Model results vs experiments for pH = 10.0

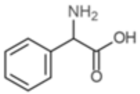
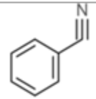
[1] D. T. Whipple, E. C. Finke, and P. J. A. Kenis, "Microfluidic Reactor for the Electrochemical Reduction of Carbon Dioxide: The Effect of pH," *Electrochem. Solid-State Lett.*, vol. 13, no. 9, p. B109, 2010.

Methodology

Half-cell reaction replacement:
Selection criteria

- At least one reaction from each group (Carboxylic acids, alcohols, aldehydes, etc.)
- Include recent progress in CO_2 electroreduction reactions and biomass oxidation for fuel production
- The result is 20 anodic and 10 cathodic reactions

A sample of selected anodic reactions

Reac. No	Reaction	Conditions
1	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	Pt, 1M, 6C±1C
2	$HCOO^- \rightarrow CO_2 + H^+ + 2e^-$	Pd, 1M, 6C±1C
3	$2\ CH_3COO^- \rightarrow CH_3CH_3 + 2CO_2 + 2e^-$	1M, pH > 4, 348K
4	2propionate$^-$ $\rightarrow C_4H_{10} + 2CO_2 + 2e^-$	Pt, 1M, pH = 7
5	methanol + $2\ H_2O \rightarrow HCO_3^- + 7\ H^+ + 6e^-$	pH = 7
6	ethanol + $5\ H_2O \rightarrow 2HCO_3^- + 14\ H^+ + 12e^-$	pH = 7
7	$C_3H_8O_3 + 8OH^- \rightarrow 3HCOOH + 5H_2O + 8e^-$	298 K, 1 bar
8	$C_3H_8O_3 + 2OH^- \rightarrow C_3H_6O_3 + 2H_2O + 2e^-$	298 K, 1 bar
9	Ph-CH-OH-CH$_3$ → Ph-C=O-CH$_3$ + $2e^-$ + $2H^+$	0.2 mM TEMPO, 0.5 M $NAHCO_3$
10	 HMF $+ 6OH^- \rightarrow$  FDCA $+ 4H_2O + 6e^-$	Pt, 0.3 M $NaClO_4$, pH= 10 to 13, 20 C
11	 HMF $+ 4OH^- \rightarrow$  FDCA $+ 2H_2O + 4e^-$	pH<7.0, NiFe LDH
12	 →  + $CO_2 + 4H^+ + 4e^-$	AgO, NaOH
13	$C_6H_{12}O_6 + 2OH^- \rightarrow C_6H_{12}O_7 + H_2O + 2e^-$	298 K, 1 bar
14	$CH_4 + 2OH^- \rightarrow CH_3OH + H_2O + 2e^-$	298 K, 1 bar

Results and Discussion

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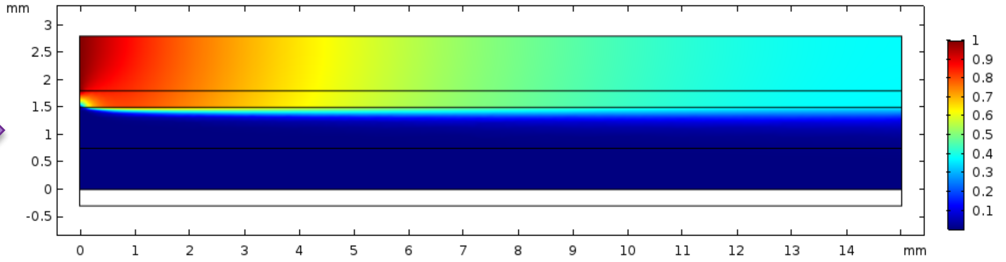
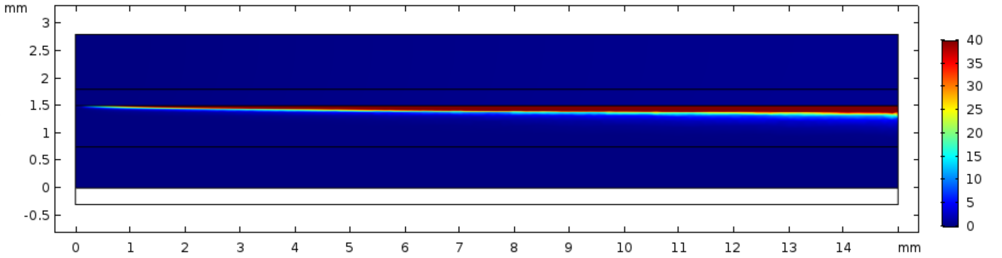
Mass transfer:

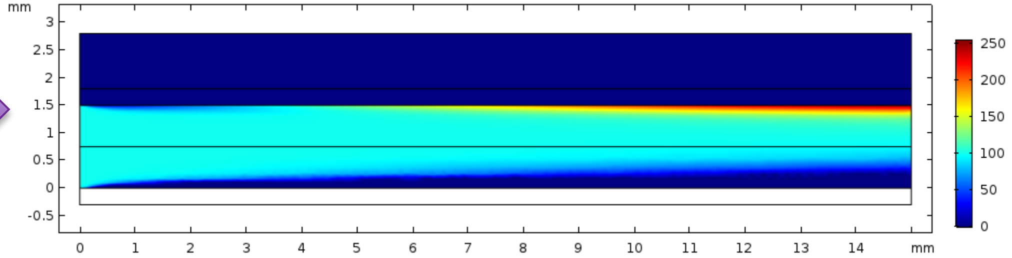
Mass fraction of CO_2



$HCOO^-$ concentration (mol/m^3)



OH^- concentration (mol/m^3)



Results and Discussion

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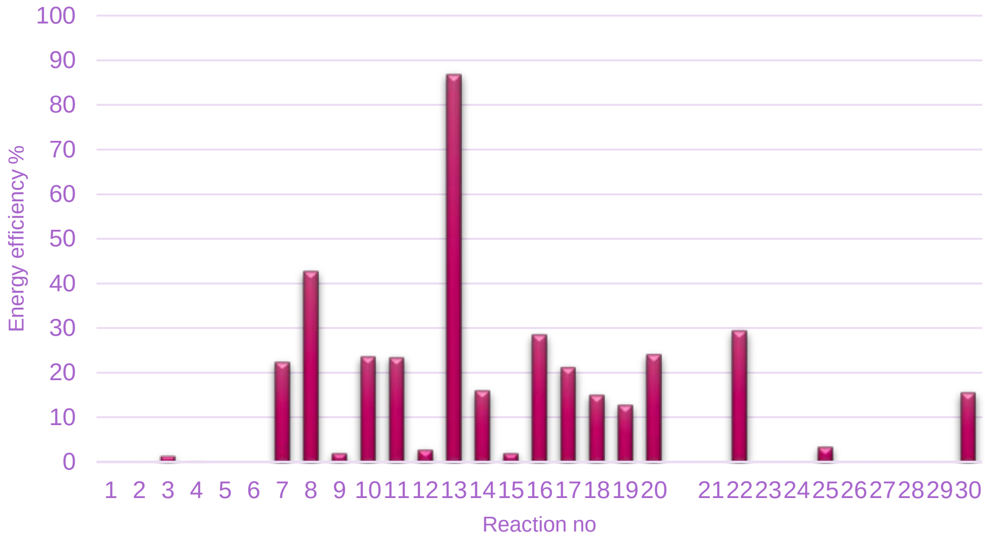
Cell energy efficiency:

$$\eta_e = \frac{Energy\ Content\ of\ the\ products\ \left[\frac{kJ}{mole}\right] \times Cell\ Fuel\ Producction\ [\frac{mole}{s}]}{VI_{cell}\ [\frac{kJ}{s}]}$$

- Cell energy efficiency changes across a wide range depending on the reaction kinetics.

- Replacing the anodic half-cell can result in up-to ~88.0 % increase in cell energy efficiency.



Energy efficiency

Results and Discussion

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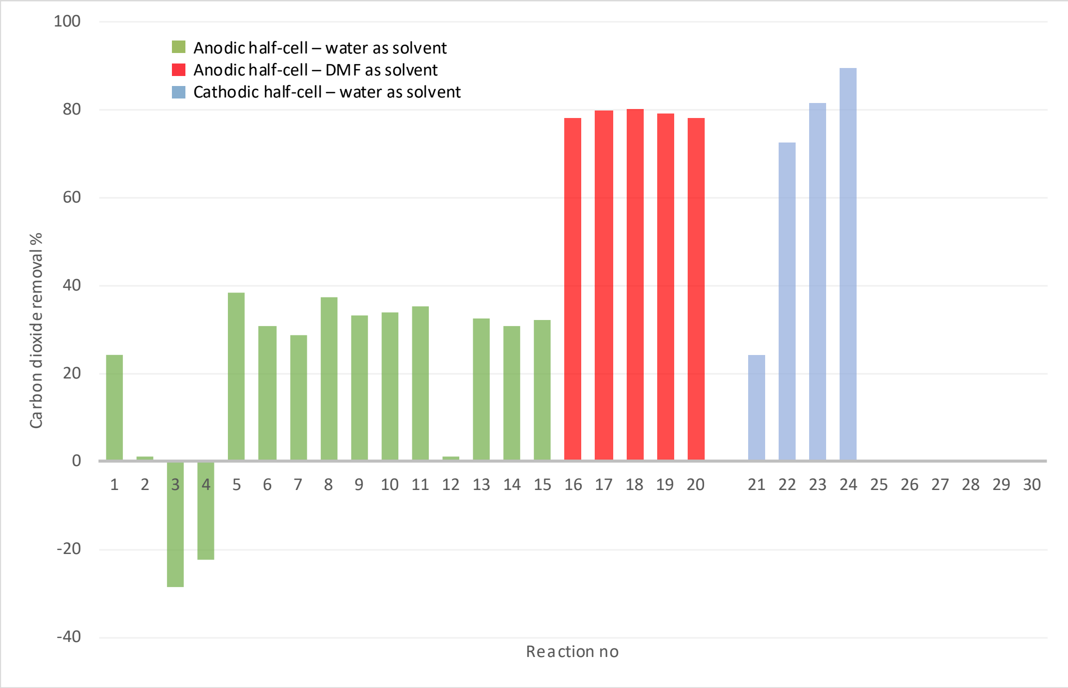
Environmental aspects:

$$X_{CO_2} = \frac{CO_2\ reacted\ [\frac{mole}{s}]}{CO_2\ fed\ [\frac{mole}{s}]}$$

- Using organic solvents result in higher overall CO_2 removal rate, due to the lack of hydrogen evolution reaction (HER) at the cathode (e.g. reactions 16-20).

- Some reactions produce CO_2 which will result in negative values (e.g. reactions 3&4). This value can also become zero when using other materials at the cathode (e.g. reactions 25 – 30).

- Replacing the anodic reactions can result in up to ~50% increase in CO_2 removal rate.



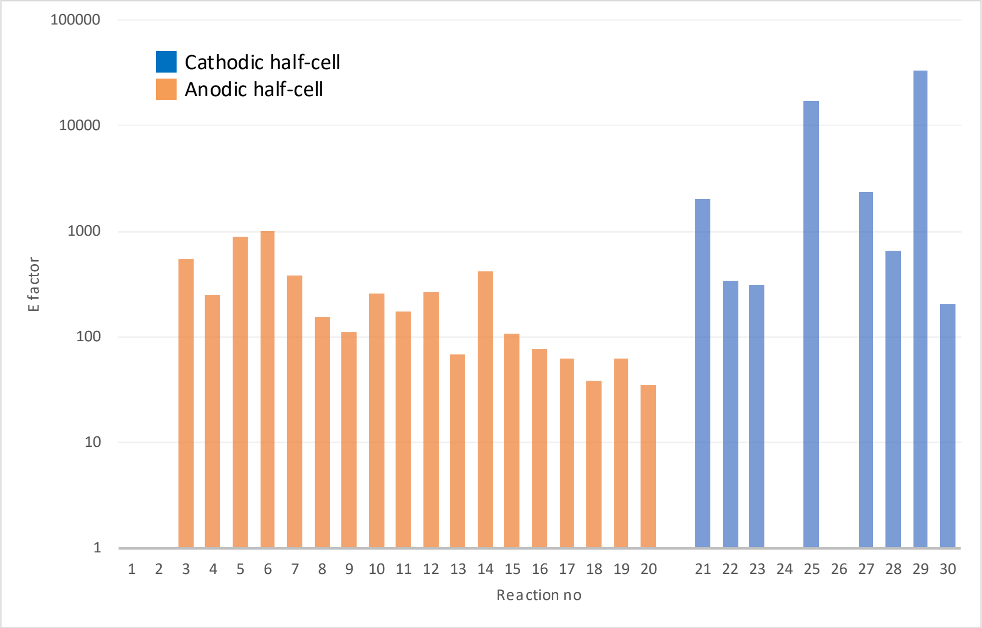
CO_2 removal rate

Results and Discussion

Environmental aspects:

$$E - factor = \frac{kgs\ of\ waste\ produced}{kgs\ of\ desired\ product}$$

- The overall E-factor is high due to the design of the studied continues-flow reactor. A large amount of solvent and reactant is flushed in the system leaving a large environmental footprint. This issue can be mitigated by optimizing the cell and recycling the solvent.



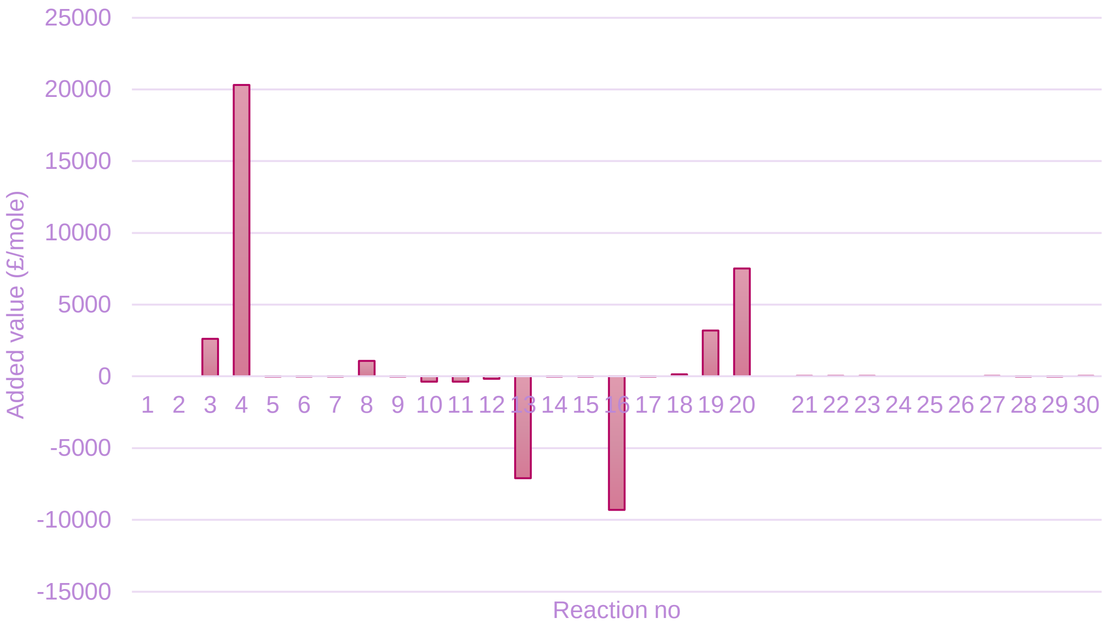
E-factor

Results and Discussion

Economical analysis:

$$added\ value\left(\frac{£}{mole}\right) = value\ of\ products\left(\frac{£}{mole}\right) - value\ of\ reactants\left(\frac{£}{\text{mole}}\right)$$

- Added value changes over a wide range and can reach up to ~20,000 £/mole if the product is purified to 99.9% or ~1000 £/mole if the product is purified to 80%.



Product added value (£/mole)

Conclusions and further work

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- An electrolytic cell was studied for electrosynthesis of biofuels via co-valorisation of bio-fermentation products and captured CO_2.
- Evaluate competing anodic and cathodic reactions using criteria such as cell energy efficiency, current efficiency, CO_2 removal rate, E factor and product added value.
- The cell design (e.g. electrolyte flow-rate and cell dimensions) is then optimized for each of the above scenarios.
- Design a multi-criteria decision analysis framework to evaluate e-bio-fuel production technologies (Additional PhD student has been recruited at Heriot-Watt University).

Green Finance, Energy Economics and Sustainable Conference
7 May 2020, Oxford

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Acknowledgement

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Thank you!

Any Questions?

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