



**MONASH** University

# Sustainability assessment framework for carbon capture and utilisation

Daniel Rojas Sánchez

BEng (Chemical) Hons/BSc

A thesis submitted for the degree of Doctor of Philosophy at  
Monash University in 2021

Department of Chemical Engineering  
Faculty of Engineering

*Yet it is not our part to master all the tides of the world,  
but to do what is in us for the succour of those years wherein we are set,  
uprooting the evil in the fields that we know,  
so that those who live after may have clean earth to till.*

- J.R.R. Tolkien, The Return of the King



## Copyright notice

© Daniel Rojas Sanchez 2021. Except as provided in the Copyright Act 1968, this thesis may not be reproduced in any form without the written permission of the author.

I certify that I have made all reasonable efforts to secure copyright permissions for third-party content included in this thesis and have not knowingly added copyright content to my work without the owner's permission.

# Abstract

Reducing CO<sub>2</sub> levels is paramount in tackling climate change. Carbon capture and utilisation (CCU) is a carbon mitigation mechanism that additionally recycles CO<sub>2</sub> for beneficial applications. The chemical conversion of CO<sub>2</sub> presents advantages on multiple fronts: environmentally, carbon emissions are reduced; economically, the products have market value; energetically, CCU processes can store and transport renewable energy; and in resources, the reliance on fossil fuels for transport and chemical manufacturing can be decreased. Therefore, CCU has the potential to prevent emissions while creating a shift in the anthropogenic carbon balance, acting as building block for materials and as a clean energy vector.

Notwithstanding these benefits, the sustainability of large-scale CCU application is not fully understood. Numerous technical publications report innovative technologies, while some assessments estimate the impacts of stand-alone processes. However, there is no systematic method that explores relevant technical, socio-economic, and environmental considerations of CCU systems to analyse accurately and select a suitable technology for a particular region.

This thesis provides such a method in a multi-faceted assessment shifting the resolution of analysis from a macro to micro-scale. The framework links different modelling approaches to help in the choice of a sustainable CCU technology for a specific region and quantify its potential environmental benefits. These approaches include an innovative extended input-output analysis (IOA) with multi-objective optimisation (MOO), comprehensive process modelling and simulations, rigorous life

cycle assessment (LCA), a preliminary economic evaluation, and sensitivity analyses to validate the representativeness of the results.

The proposed framework is applied to the Australian economy as a case study. The IOA model indicates that the key industrial sectors to reduce emissions are agriculture and energy supply. The overlap of their value chains and large-scale CCU conversion pillars narrows the focus to ethanol production. A promising CCU pathway to produce ethanol is the electroreduction of  $\text{CO}_2$ , which substitutes the need of agricultural feedstock for waste  $\text{CO}_2$ . An LCA on a state-of-the-art electrolyser coupled with an innovative model for product separation compares its impacts with the traditional fermentation of crops. The assessment proves ethanol via this novel system can offer comparable or improved environmental impacts, especially in reduced water consumption and land footprint. Its modular configuration allows its application in remote areas with available renewable energy, leveraging existing infrastructure for storage and distribution of carbon-based fuels. Without the need of agricultural systems, this process has the potential to offer a viable carbon-neutral and long-term solution to sustainable biofuel generation.

The framework presented demonstrates the capability of modelling techniques paired with mathematical algorithms and publicly-available data to extract valuable insights. It uncovers the benefits of an early-stage CCU technology against a bio-based reference, which is essential as fossil fuels gradually become obsolete. It also identifies areas of improvement and further focus that are crucial in the future scaling of this technology. In general, this systematic framework addresses fundamental parameters to be considered for assessing sustainable CCU applications in context. It ultimately provides more understanding on the full impact of using CCU as a carbon abatement mechanism and endorses further development for its widespread use.

# Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Signature: .....

Print Name: Daniel Rojas Sanchez

Date: .....

# Publications during enrolment

## Journal papers:

Rojas Sanchez, D, Hoadley, AFA, & Khalilpour, KR 2019, ‘A multi-objective extended input – output model for a regional economy’, *Sustainable Production and Consumption*, vol. 20, pp. 15–28

Rojas Sanchez, D, Khalilpour, KR, & Hoadley, AFA 2021, ‘How sustainable is CO<sub>2</sub> conversion to ethanol? – a life cycle assessment of a new electrocatalytic carbon utilisation process’, *Manuscript submitted for publication*

## Peer-reviewed conference papers:

Rojas Sanchez, D & Halupka, V 2020, ‘Building a successful Engineering Student Team, recommendations from a student leader’s perspective’ in *Proceedings of the Australasian Association for Engineering Education 2020 31st Annual Conference*, Sydney.

# Acknowledgements

Undertaking this PhD has been an exciting, terrifying, rewarding, frustrating, and memorable adventure. Overall, this research project took three and a half years, many of my first grey hairs, and an invaluable set of experiences and lessons. On this path, many of those close to me have contributed to the cause -for the better or the worse- and I am thankful to every single one of them.

I express my deepest gratitude and recognition to my supervisors, Andrew Hoadley and Kaveh Khalilpour. With Kaveh's insightful perspectives and Andrew's rigorous expertise, I think we made quite a good team. Thank you both for your constant support in this joint road of discovery and learning. It was a privilege to have had you as supervisors and mentors.

Lisanna, you were my foundation in every single connotation of the word. Thank you for helping me move forward in the most difficult times, for showing me unconditional love and support, and for your patience throughout the journey. I cannot wait to start the next chapter of our lives together.

To all my friends and colleagues, who provided endless reasons to delay my work but made every part of it so enjoyable – thank you, it made all the difference.

In addition, I extend my sincere appreciation to Monash University for granting the scholarships that allowed me to undertake this research and for promoting the development of student teams such as Monash BrewLab. Although working on it took more time than I would like to make public, it will remain one of my favourite aspects of my time here.

Above all, I thank my parents. Everything I am right now is a result of you. Although you were on the other side of the world, you were present every step of the way. As you gave me all the means and tools to get to this point, this thesis is in your honour.

# Contents

ABSTRACT.....	IV
DECLARATION .....	VI
PUBLICATIONS DURING ENROLMENT .....	VII
ACKNOWLEDGEMENTS.....	VIII
CONTENTS.....	IX
LIST OF FIGURES .....	XIV
LIST OF TABLES .....	XVII
NOMENCLATURE AND ABBREVIATIONS.....	XIX
<b>1 INTRODUCTION .....</b>	<b>1</b>
1.1 RESEARCH AIMS.....	4
1.2 OUTLINE OF THESIS .....	5
<b>2 LITERATURE REVIEW .....</b>	<b>8</b>
2.1 INTRODUCTION.....	9
2.2 CO <sub>2</sub> SOURCES.....	9
2.3 CARBON CAPTURE TECHNOLOGIES.....	11
<i>2.3.1 Carbon capture and storage .....</i>	<i>13</i>
2.4 CARBON UTILISATION PATHWAYS .....	15
<i>2.4.1 Chemical uses of CO<sub>2</sub> .....</i>	<i>16</i>
2.5 POTENTIAL LARGE-SCALE AREAS OF UTILISATION.....	17
<i>2.5.1 Conversion to synthetic hydrocarbons and fuels .....</i>	<i>18</i>
2.6 RENEWABLE ENERGY .....	19
2.7 LIFE CYCLE ASSESSMENT.....	21
<i>2.7.1 Methodological guidelines .....</i>	<i>22</i>
2.8 ADDITIONAL CONSIDERATIONS IN CCU ASSESSMENTS.....	24
2.9 FUNCTIONAL COMMERCIAL OR PILOT-SCALE PLANTS .....	27

2.10 CONCLUSIONS .....	30
<b>3 NATIONAL LEVEL ANALYSIS, EXTENDED INPUT-OUTPUT ANALYSIS.....</b>	<b>32</b>
3.1 BACKGROUND.....	33
3.1.1 <i>Input-output analysis</i> .....	33
3.1.2 <i>Global warming potential</i> .....	36
3.1.3 <i>Characterisation metrics and time horizon selection</i> .....	36
3.2 MODELLING FRAMEWORK .....	38
3.2.1 <i>Input-Output Model</i> .....	39
3.2.2 <i>Sectoral Analysis</i> .....	41
3.2.3 <i>Multi-objective optimisation</i> .....	44
3.3 CASE STUDY OF THE AUSTRALIAN ECONOMY .....	46
3.3.1 <i>Background and literature review</i> .....	46
3.3.2 <i>Data considerations</i> .....	47
3.3.3 <i>Results of sectoral analysis</i> .....	48
3.3.4 <i>Bi-objective optimisation</i> .....	58
3.3.5 <i>Tri-objective optimisation</i> .....	62
3.3.6 <i>Discussion</i> .....	65
3.4 CONCLUSIONS .....	67
<b>4 METHODOLOGY, LIFE CYCLE ASSESSMENT.....</b>	<b>70</b>
4.1 BACKGROUND.....	71
4.1.1 <i>Life cycle assessment</i> .....	71
4.1.2 <i>Life cycle assessment for carbon capture and utilisation</i> .....	73
4.2 MODELLING FRAMEWORK .....	74
4.2.1 <i>Goal and scope definition</i> .....	75
4.2.1.1 CCU technology selection.....	78
4.2.2 <i>Inventory considerations</i> .....	79
4.2.2.1 Considerations for low TRL CCU pathways.....	81
4.2.3 <i>Impact assessment methodology</i> .....	82
4.3 CASE STUDY APPLICATION .....	83
4.3.1 <i>Selection of process to evaluate</i> .....	83
4.3.2 <i>Ethanol</i> .....	84



4.3.3 Ethanol production via CCU .....	85
4.3.4 Electrocatalytic reduction of CO <sub>2</sub> .....	86
4.3.4.1 CO <sub>2</sub> RR to ethanol.....	87
4.3.5 Environmental assessments of CO <sub>2</sub> RR process designs.....	88
4.3.6 Proposed system .....	89
4.3.6.1 Geographical considerations .....	90
4.3.7 Process modelling for proposed ECCR system.....	90
4.3.7.1 Direct air capture unit.....	92
4.3.7.2 Electrolyser stack.....	93
4.3.7.3 Adsorption system .....	101
4.3.7.4 Distillation system .....	107
4.3.7.5 Integrated ECCR system.....	116
4.4 CONCLUSIONS.....	117
<b>5 RESULTS, LIFE CYCLE ASSESSMENT.....</b>	<b>119</b>
5.1 LCA RESULTS CONSIDERATIONS.....	120
5.1.1 Uncertainty and sensitivity analysis .....	120
5.1.2 Normalisation, weighting, and endpoint categories .....	121
5.2 CASE STUDY OF ETHANOL PRODUCTION VIA ELECTROCATALYTIC REDUCTION OF CAPTURED CO <sub>2</sub>	122
5.2.1 Goal and scope .....	123
5.2.2 Life cycle inventory and scenarios .....	125
5.2.2.1 ECCR system.....	126
5.2.2.2 Reference production system .....	127
5.2.2.3 Electricity input scenarios .....	131
5.2.3 Life cycle impact assessment.....	132
5.2.4 Results .....	133
5.2.5 Electrolyser sensitivity analysis .....	143
5.2.6 Discussion.....	150
5.3 INTERPRETATION AND CONCLUSIONS.....	153
<b>6 DISCUSSION OF THE SYSTEMATIC APPROACH.....</b>	<b>155</b>
6.1 PRELIMINARY ECONOMIC EVALUATION.....	156
6.2 ENVIRONMENTAL CONSIDERATIONS .....	163
6.2.1 Parameter uncertainty.....	163

6.2.2 Model uncertainty .....	164
6.2.3 Uncertainty due to choices.....	167
6.2.3.1 Multifunctionality solution.....	167
6.2.3.2 System boundaries .....	175
6.3 SOCIAL CONSIDERATIONS AND POLICY-MAKING.....	177
6.3.1 Social perception of CCU .....	179
6.4 FINAL DISCUSSION .....	180
6.4.1 Case study .....	181
6.4.2 Scaling.....	184
6.5 CONCLUSIONS .....	185
<b>7 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK.....</b>	<b>187</b>
7.1 CONTRIBUTIONS OF RESEARCH .....	187
7.2 CASE STUDY CONCLUSIONS.....	190
7.3 FUTURE WORK .....	192
<b>REFERENCES .....</b>	<b>195</b>
<b>APPENDIX A .....</b>	<b>220</b>
<b>APPENDIX B .....</b>	<b>224</b>
GENERAL INVENTORY CONSIDERATIONS.....	224
B1. ELECTROLYSER STACK .....	225
B1.1 Manufacture of assembled electrolyser .....	226
B1.2 Manufacture of N-C/Cu electrode.....	228
B1.3 Manufacture of Ni foam catalyst.....	230
B1.4 Manufacture of anion exchange membrane .....	231
B1.5 Manufacture of the gas diffusion layer .....	233
B1.6 Manufacture of electrolyte.....	236
B1.7 Manufacture of Fe-Co composite film on carbon fibre paper electrode.....	237
B2. DIRECT AIR CAPTURE SYSTEM .....	239
B3. ADSORPTION SYSTEM .....	242
B4. ETHANOL PRODUCTION BY ECCR SYSTEM.....	244
B5. ETHANOL PRODUCTION BY THE BIOETHANOL BENCHMARK SYSTEM.....	246
B6. HIGH AND MEDIUM VOLTAGE ELECTRICITY .....	249

B7.	DISTILLATION UNIT SIMULATION STREAM TABLE.....	250
B8.	THEORETICAL ENERGY REQUIREMENTS CALCULATION.....	254
B9.	ADDITIONAL PLOTS .....	256

# List of figures

Fig. 1.1 General scope and narrative of research with outline of thesis chapters. ....	6
Fig. 2.1 Global CO <sub>2</sub> emissions by sector in 2018. ‘Other’ includes commercial and public services, agriculture/forestry, fishing and non-specified final energy consumption. Bar plot on the right reallocates the electricity and heat of Power generation to the sector where it is ultimately consumed. Data from IEA (2020c).....	10
Fig. 3.1 Simplified visual representation of the data arrangement in the extended IO table.....	40
Fig. 3.2 Ranked lists of Sectoral Production, Value-added, and Employment multipliers.....	49
Fig. 3.3 Distribution of sectors in four quadrants based on their index of the power of dispersion (IPD) and the index of the sensitivity of dispersion (ISD).....	52
Fig. 3.4 Ranked lists of greenhouse emission coefficients ( $e$ ) and greenhouse emission multipliers (GHEM). Units are tonnes of CO <sub>2</sub> -e per one thousand USD worth of output and final demand, respectively.....	53
Fig. 3.5 Greenhouse gas emissions on a producer (left) vs a consumer (right) perspective.....	55
Fig. 3.6 Distribution of sectors in quadrants based on their greenhouse input ratio (GHIR) and greenhouse output ratio (GHOR).....	58
Fig. 3.7 Pareto front, GDP vs Total emissions.....	59
Fig. 3.8 Interaction between emission reduction, GDP achieved [in billion USD and percentage of original GDP level] (left axes, thick dark blue curve) and unitary GDP loss [USD per kg CO <sub>2</sub> -e reduced] (right axis, thin light blue curve).....	62
Fig. 3.9 3-D representation of optimal solution polyhedron with 2-D projections. Vertices and lines are optimal points; grey surfaces are areas of weakly efficient points.....	65
Fig. 4.1 Stages of an LCA framework as described in the ISO 14040 series.....	73
Fig. 4.2 Decision tree for selecting the functional unit of an LCA involving a CCU technology. Adapted from decision tree in Zimmerman <i>et al.</i> (2018).....	76
Fig. 4.3 Comparison between different methods to solve multi-functionality in CCU. System expansion, system expansion by substitution, and allocation .....	78
Fig. 4.4 Selection of CCU potential processes for assessment in a particular region .....	79
Fig. 4.5 Illustrative background and foreground processes in an LCA inventory .....	80
Fig. 4.6 Process flow chart of the electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system. G/L = gas/liquid. VSA = vacuum swing adsorption.....	92
Fig. 4.7 Carbonate equilibria results validation against data reported by Gupta <i>et al.</i> (2006).....	99
Fig. 4.8 Schematic of adsorption cycles in dual-bed system.....	106
Fig. 4.9 Process flow diagram of the distillation unit simulation. Full stream table in Appendix (Table B18).....	109
Fig. 4.10 Composite curves for the heat integration showing utilities and pinch point.....	115

Fig. 4.11 Grand composite curve indicating required heating and cooling requirements.....	115
Fig. 4.12 Material and energy flows in the entire electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system .....	116
Fig. 5.1 Comparison of ethanol production via electrocatalytic captured CO <sub>2</sub> reduction (ECCR) and via the reference process of crop fermentation.....	124
Fig. 5.2 Process flow chart and system boundaries of the electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system.....	125
Fig. 5.3 System boundaries of the reference sorghum bioethanol system.....	128
Fig. 5.4 Map of Australia with the state of Queensland highlighted (left image) and map of regions of sorghum source for Dalby Biorefinery (orange triangle): Western Downs (1, green area), Darling Downs (2, blue), and northern zone of New South Wales (3, grey) (right image). Images under Creative Commons license.....	130
Fig. 5.5 Potential environmental impacts in all categories of the electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system at the High, Mid, and Low carbon intensity electricity scenarios and the reference system of sorghum bioethanol.....	134
Fig. 5.6 Carbon footprint of ethanol production by the electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system (dark blue line) and by the sorghum reference (light green line) with electricity of different sources and carbon intensity. <i>Icons taken from open-source websites icons8.com and cleanpng.com....</i>	137
Fig. 5.7 Carbon footprint of ethanol production by ECCR (blue line), by sorghum using only electricity (orange line), and by the reference sorghum process (dotted green line) with electricity of different sources and carbon intensity. <i>Icons taken from open-source websites icons8.com and cleanpng.com....</i>	138
Fig. 5.8 Sensitivity analysis for water consumption, land use, and global warming using different sorghum sources.....	140
Fig. 5.9 Potential environmental impacts in all categories for the electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system and sorghum bioethanol (S) using electricity from the three different scenarios (High, Mid, Low) and the fully electric bioethanol process using Low-CI electricity (S Low E).....	142
Fig. 5.10 Relative contribution of the subcomponents of the electrolyser (assembly, cathode, anode, and electrolyte) to the examined environmental impact categories.....	144
Fig. 5.11 Effect of the PTFE membrane of the cathode to the ozone depletion potential compared to the reference. The range of PTFE membrane thickness is 10 – 270 µm.....	145
Fig. 5.12 Relative comparison in environmental impacts with the electrolyser using a Ni foam anode and a Fe-Co anode.....	146
Fig. 5.13 Sensitivity analysis on the effect of the lifetime of the catalyst in the ECCR system using the Low-CI scenario for all examined environmental impact categories. The range of the lifetime is 60,000 hours, 10,000 hours, 5,000 hours, 2,500 hours, and 500 hours .....	148
Fig. 5.14 Sensitivity analysis on the effect of the lifetime of the catalyst in the ECCR system cathode using High and Low carbon intensity (High-CI and Low-CI) electricity scenarios for all examined environmental impact categories. Bars show impact at a lifetime of 5,000 hours with error bars for a lifetime of 500 hours to 60,000 hours. With the exception of ozone layer depletion (ODP), the difference between the impact of 5,000- and 60,000-hours catalyst lifetime is marginal.....	149

Fig. 5.15 Relationship between the lifetime of the cathode and the global warming potential of ethanol via the electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system.....	150
Fig. 6.1 Upper limit capital investment for return on investment according to the price of electricity..	159
Fig. 6.2 Upper limit cost of equipment of the entire electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system at manufacturer's site according to the price of electricity with different levels of carbon credit161	
Fig. 6.3 Historical costs of alkaline electrolyzers and the threshold value of breakeven for the cost of equipment of the ECCR system. Numbers indicate the references for each point, detailed in Table 6.2162	
Fig. 6.4 Difference in the global warming potential of the ECCR system at the different carbon intensity scenarios and the sorghum reference with characterisation values for a 100 and 20-year horizons.....	166
Fig. 6.5 Carbon footprint of ethanol production by ECCR (blue line) and by the sorghum reference (green line) using a global warming potential characterisation factor based on a 20-year horizon (continuous line) and a 100-year horizon (dash-dotted line) with electricity of different sources and carbon intensity. <i>Icons taken from open-source websites icons8.com and cleanpng.com.....</i>	167
Fig. 6.6 Change in impact of bioethanol production by sorghum fermentation at all examined environmental impact categories using different cottonseed meal and soybean meal as DDGS substitute for system expansion.....	170
Fig. 6.7 Potential environmental impacts in all categories of the electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system at the High, Mid, and Low carbon intensity electricity scenarios and reference sorghum bioethanol system using allocation (all) and system expansion with cottonseed meal (Cot) and soybean meal (Soy) .....	173
Fig. 6.8 Carbon footprint of ethanol production by electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system, by sorghum fermentation with allocation, and by sorghum fermentation with system expansion using canola meal, cottonseed meal, and soybean meal to substitute the coproduction of dry distiller's grains with solubles (DDGS), with electricity of different sources and carbon intensity. <i>Icons taken from open-source websites icons8.com and cleanpng.com.....</i>	174
Fig. 6.9 Global warming potential of ethanol production via electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system, via sorghum fermentation modelled through allocation and substitution (using average of cottonseed meal and soybean meal results), including emissions from combustion .....	176
Figure B1. Process flowchart of theoretical conversion and separation. Composition percentages are mole fractions. The ethanol product is 95% m/m or 88% mol/mol .....	255
Figure B2. Potential environmental impacts in all categories for the electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system, sorghum bioethanol, and the ECCR system with the Fe-Co anode substitute, using electricity from the three different scenarios (High, Mid, Low) .....	256
Figure B3. Carbon footprint of ethanol production by ECCR using a Fe-Co anode (continuous blue line) and a Ni foam anode (dotted blue line), and by sorghum using only electricity (orange continuous line) and by the reference sorghum process (dotted green line) with electricity of different sources and carbon intensity.....	257

# List of tables

Table 2.1 CO <sub>2</sub> concentration in volume from streams of various sources prior to capture.....	13
Table 4.1 Characteristics of electrolyser .....	94
Table 4.2 Main reactions in system.....	95
Table 4.3 Carbonate equilibria parameters in function of temperature (T).....	97
Table 4.4 Sechenov equation parameters.....	98
Table 4.5 Dual-site Langmuir parameter fits for CO <sub>2</sub> and C <sub>2</sub> H <sub>4</sub> in Activated Carbon .....	104
Table 4.6 Properties of inlet stream and bed.....	104
Table 4.7 Duty for heat exchangers in distillation unit .....	112
Table 4.8 Overview of simulation assumption values.....	113
Table 4.9 Carbon balance of system including recycled streams.....	117
Table 4.10 Carbon balance of system with only inputs and outputs.....	117
Table 5.1 Inventory of ethanol production via the electrocatalytic captured CO <sub>2</sub> reduction (ECCR) system. ( <i>Details provided in Appendix section B1</i> ) .....	127
Table 5.2 Inventory for reference sorghum bioethanol production. ( <i>Details provided in Appendix section B5</i> ).....	129
Table 5.3 Electricity scenarios according to carbon intensity of grid by their fuel breakdown. CCGT: combined cycle gas turbine; OCGT: Open cycle gas turbine.....	131
Table 5.4 Percentage reduction in all examined environmental impact categories of ethanol production via ECCR in every carbon intensity (CI) electricity scenario when using the Fe-Co anode compared to using the Ni foam anode. Intensity of colour indicates a higher reduction.....	147
Table 6.1 Prices and operational costs of inputs and outputs of ECCR system.....	158
Table 6.2 References for points and ranges in Figure 6.3.....	162
Table 6.3 Protein quality for sorghum dry distiller's grains with solubles (DDGS), cottonseed meal, and soybean meal.....	168
Table B1. Inventory for the electrolyser stack.....	226
Table B2. Inventory for the assembled electrolyser.....	228
Table B3. Inventory for the manufacture of N-C/Cu electrode.....	229
Table B4. Inventory for the manufacture of Ni foam.....	231
Table B5. Inventory for the manufacture of the anion exchange membrane.....	233
Table B6. Inventory for the manufacture of the gas diffusion layer.....	234
Table B7. Inventory for the production of carbon fibre.....	235
Table B8. Inventory for the production of acrylic fibre.....	236

Table B9. Inventory for the production of KOH 1M electrolyte .....	237
Table B10. Manufacture of Fe-Co composite film electrode .....	238
Table B11. Inventory for the Direct Air Capture plant.....	240
Table B12. Inventory of captured CO <sub>2</sub> from Direct Air Capture .....	241
Table B13. Inventory for the adsorption system.....	243
Table B14. Inventory of ethanol production via the ECCR system .....	245
Table B15. Inventory of bioethanol production via sorghum fermentation.....	248
Table B16. Inventory for high voltage electricity generation.....	249
Table B17. Inventory for medium voltage electricity generation.....	249
Table B18. Full stream table of the converged distillation simulation model.....	250
Table B19 Energy requirements of each block in theoretical process flowchart.....	255



# Nomenclature and abbreviations

## Upper-case

$A$	Technical coefficient matrix (input-output analysis)
$A$	Electrode area (equation 4.2)
ABS	Australian Bureau of Statistics
AC	Activated Carbon
ADP	Abiotic Depletion Potential
AEM	Anion Exchange Membrane
AEMO	Australian Energy Market Operator
ANZSIC	Australian and New Zealand Standard Industrial Classification
AP	Acidification Potential
AR5	Fifth Assessment Report
ARENA	Australian Renewable Energy Agency
AU	Australia
AUD	Australian Dollars
$B_i$	Capital cost parameter (preliminary economic evaluation)
BREE	Bureau of Resources and Energy Economics
CAPEX	Capital Expenditure
$C_{BM}$	Cost of Bare Module
CCGT	Combined Cycle Gas Turbine
CCR	Carbon Capture and Recycling/Re-use
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilisation
CCUS	Carbon Capture, Utilisation and Storage
CDU	Carbon Dioxide Utilisation
CF	Capacity Factor
CFC	Chlorofluorocarbons
$C_{FCI}$	Cost of Fixed Capital Investment
CFP	Carbon Fibre Paper
CI	Carbon Intensity
CMME	Chloromethylmethylether

CNG	Compressed Natural Gas
CO <sub>2</sub> e	Carbon dioxide equivalent
CO <sub>2</sub> RR	Carbon Dioxide Reduction Reaction
CO <sub>2</sub> RX	CO <sub>2</sub> consumption rate
<i>CoP</i>	Coefficient of Performance
CP	Carbon Paper
<i>C<sub>P</sub></i>	Cost of equipment
CRF	Capital Recovery Factor
CRI	Carbon Recycling International
CSIRO	Commonwealth Scientific and Industrial Research Organisation
<i>C<sub>TCI</sub></i>	Total Capital Investment
<i>C<sub>TM</sub></i>	Cost of Total Module
DAC	Direct Air Capture
DB	Dalby Biorefinery
DC	Design Capacity
DDGS	Dry Distiller's Grains with Solubles
DM	Dry Matter
DMA	Dimethylacetamide
DME	Dimethyl Ether
<i>E<sub>A</sub></i>	Activation Energy of component A
ECCR	Electrocatalytic captured CO <sub>2</sub> reduction
E <sub>CO<sub>2</sub>RR</sub>	Applied potential for CO <sub>2</sub> reduction reaction
EDC	Ethylene Dichloride Catalyst
EEIO	Environmentally-Extended Input-Output
EM	Employment Multiplier
EOR	Enhanced Oil Recovery
EP	Eutrophication Potential
EPD	Environmental Product Declaration
ETL	Emissions-to-Liquids
EU	European Union
<i>F</i>	Emissions matrix (input-output analysis)
<i>F</i>	Faraday constant
FE	Faradaic Efficiency
FPMF	Fine Particulate Matter Formation
GDL	Gas Diffusion Layer

GDP	Gross Domestic Product
GHEM	Greenhouse Emission Multiplier
GHG	Greenhouse Gas
GHIR	Greenhouse Input Ratio
GHOR	Greenhouse Output Ratio
GLO	Global
GTL	Gas-to-Liquids
GTP	Global change in Temperature Potential
GWP	Global Warming Potential
HEX	Heat Exchanger
HFC	Hydrofluorocarbons
$I$	Identity matrix
IAST	Ideal Adsorbed Solution Theory
IEA	International Energy Agency
IEAGHG	International Energy Agency Greenhouse Gas R&D Programme
IO	Input-Output
IOA	Input-Output Analysis
IPCC	Intergovernmental Panel on Climate Change
IPD	Index of the Power of Dispersion
IRENA	International Renewable Energy Agency
IRF	Impulse Response Function
ISD	Index of the Sensitivity of Dispersion
ISIC	International Standard Industrial Classification
ISO	International Organization for Standardization
KP	Kyoto Protocol
$K_s$	Sechenov constant
$L$	Leontief inverse matrix (input-output analysis)
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LCOP	Levelised Cost of Product
LNG	Liquefied Natural Gas
LP	Linear Programming
LPG	Liquefied Petroleum Gas
LU	Land Use

LULUCF	Land Use and Land Use Change and Forestry
MEA	Monoethanolamine
MOLP	Multi-Objective Linear Programming
MOO	Multi-Objective Optimisation
MPL	Microporous Layer
NEM	National Electricity Market
NETL	National Energy Technology Laboratory
NSW	New South Wales
OCGT	Open Cycle Gas Turbine
ODP	Ozone Depletion Potential
OECD	Organisation for Economic Co-operation and Development
OER	Oxygen Evolution Reaction
OPEX	Operating Expenditure
$P$	Objective function matrix (equation 3.13)
$P$	Pressure
P2G	Power-to-Gas
P2X	Power-to-X
PCC	Post-Combustion Capture
$P_{CO_2}$	Partial pressure of CO <sub>2</sub>
PEF	Product Environmental Footprint
PFC	Perfluorocarbons
$P_H$	High adsorption Pressure
$P_L$	Low adsorption Pressure
PMFP	Particulate Matter Formation Potential
POCP	Photochemical Ozone Creation Potential
PSA	Pressure Swing Adsorption
PTFE	Polytetrafluoroethylene
PV	Photovoltaic
$Q_i$	Molar flowrate of chemical $i$
QLD	Queensland
$R$	Ideal gas constant
RE	Renewable Energy
RHE	Reversible Hydrogen Electrode
$S$	n-dimensional polyhedron of feasible points (input-output analysis)

SDG	Sustainable Development Goals
SETAC	Society of Environmental Toxicology and Chemistry
SMR	Steam Methane Reforming
SPM	Sectoral Production Multiplier
SS	Stainless steel
$T$	Temperature
TRL	Technology Readiness Level
UK	United Kingdom
UN	United Nations
UNFCCC	United National Framework Convention on Climate Change
US	United States
USD	United States Dollars
$V$	Volume (equation 4.24)
VAM	Value-Added Multiplier
VLP	Vector Linear Program
VSA	Vacuum Swing Adsorption
WC	Water Consumption
WIOD	World Input-Output Database
$Z$	Transaction or inter-industry matrix (input-output analysis)

## Lower case

$a$	Technical or direct input coefficient (input-output analysis)
$b_A$	Langmuir parameter for component A
$e$	Greenhouse gas emissions coefficient vector (input-output analysis)
$f$	Emissions per sector matrix (input-output analysis)
$j_i$	Partial current density of chemical $i$
$j_T$	Total current density
$l$	lower bound on demand (equation 3.14)
$m$	Imports matrix (input-output analysis)
$m_{ads}$	Mass of adsorbent
$\dot{n}$	Molar flowrate entering adsorption bed
$p$	Pressure (equation 4.19)
$q_A$	Working capacity of bed for component A
$s$	Social account matrix (input-output analysis)

$t_{b,i}$	Time till breakthrough of component $i$
$t_c$	Time of cycle
$t_{c,ss}$	Time till cyclic steady-state
$t_{d,i}$	Time till depletion of component $i$
$t_{ss}$	Time till steady-state
$u$	upper bound on demand (equation 3.14)
$v_a$	Value-added matrix (input-output analysis)
$x$	Total output vector (input-output analysis)
$x$	Stoichiometric coefficient for ethanol in global cell reaction (equation 5.4)
$y$	Final demand matrix (input-output analysis)
$y$	Stoichiometric coefficient for ethylene in global cell reaction (equation 5.4)
$y_0$	Original levels of final consumption (equation 3.15)
$y_i$	Vapour fraction of component $i$ (equation 4.24)
$z$	Transaction matrix internal flow (input-output analysis)

## Greek letters

$\alpha$	Satisfaction ratio for final demand (equation 3.15)
$\alpha_i$	Number of electrons in reduction reaction (equation 4.2)
$\alpha_i$	Capital cost parameter (preliminary economic evaluation)
$\varepsilon$	Emissions target
$\sigma$	Value added coefficients vector
$\phi^0$	Emissions in production of own products in sector
$\phi^C$	Emissions in production of own products by other sectors
$\phi^P$	Emissions in production of products for other sectors

# 1 Introduction

The current climate crisis is widely accepted to be linked to anthropogenic activity (IPCC 1990). Global warming is at the forefront of this climate change panorama, attributed to greenhouse gas (GHG) emissions. The Paris Agreement is the latest international driver to reduce GHG emissions, with an aim to maintain global temperature rise well below 2°C pre-industrial levels (UNFCCC 2015). However, the Intergovernmental Panel on Climate Change (IPCC) determined that an increase of more than only 1.5°C would have catastrophic consequences (IPCC 2018). Recently, the Australian Academy of Science (2021) quantified the consequences of a 3°C temperature rise for the country -which is the current projected temperature rise by 2100- and detailed the devastating consequences of the associated climate change.

In any attempt to keep global temperature rise under 1.5°C, not only do GHG emissions need to be reduced but also entire value chains have to adapt to support human activity with net-zero emissions (Rogelj et al. 2018). During the next decade, it will be necessary to create a rapid decarbonisation across all regions and the sectors within them. Carbon capture is one of the tools that has been regarded as instrumental in the joint effort to achieve such decarbonisation (IEA 2017).

Initially, carbon capture and storage (CCS) was of much interest, offsetting carbon emissions by storing captured CO<sub>2</sub> underground. However, few storage sites have been confirmed to offer a permanent and safe containment (Global CCS Institute 2020). The associated risk, high investment costs, and low public acceptance have stalled the deployment of CCS (Daggash et al. 2018). Thus, interest has increasingly shifted towards carbon capture and utilisation (CCU), taking advantage of cheap

renewable energy to make use of the captured CO<sub>2</sub> rather than store it as waste (Pekdemir 2015) and improve the economic viability of carbon removal (Markewitz et al. 2012).

The development of different CCU pathways has provided a wide range of techniques to employ CO<sub>2</sub> physically or chemically (Rafiee et al. 2018). The chemical conversion of CO<sub>2</sub> presents advantages on multiple fronts: economically, the market value of the products made from these processes offers a financial incentive (Styring et al. 2011); energetically, CCU processes can be used to convert surplus renewable energy into products that are easier to store and transport (Rihko-Struckmann et al. 2010); environmentally, the carbon emissions are directly and indirectly reduced (Aresta et al. 2013); and in terms of resources, it can help in decreasing the reliance on fossil fuels for energy and chemical manufacturing (Otto et al. 2015). Therefore, CCU has the potential to prevent emissions, balance the anthropogenic carbon cycle, function as feedstock for other chemicals, and act as a vector of renewable energy.

CCU is energy-intensive and can be related to complex value-chains, so the aforesaid benefits may not be guaranteed for every process (Sakakura et al. 2007). Its environmental benefits are a function of important parameters such as the source of the energy supplied to the process (Al-Kalbani et al. 2016). Additionally, its ultimate effect might not have the expected outcome in the interrelated configuration of an economy (Peters et al. 2011). Therefore, comprehensive assessments are required to determine the overall sustainability and suitability of each CCU case.

Although techno-economic and environmental modelling approaches are able to analyse particular technologies, there is no complete systematic framework to select and analyse a suitable CCU technology for a specific region. Numerous technical publications report innovative materials or designs for increased efficiencies in specific technologies (Ma et al. 2019), while several environmental assessments estimate the impacts of particular processes (Dominguez-Ramos et al. 2015; Hoppe et al. 2018; Koj



et al. 2015; Sternberg et al. 2017). However, there is a gap in a systematic method capable of exploring key areas of opportunity at a large scale, identifying an optimal CCU pathway for a region and focusing on its detailed scrutiny.

Moreover, in the case of CCU technologies in early development, data to conduct the required assessments is incomplete or inaccurate. The technology readiness level (TRL) is a metric of technical maturity of any type of technology (Héder, 2017). In low TRL systems, critical aspects such as auxiliary processes, production separation, or heat integration are rarely considered (Sánchez et al. 2020). Thus, there is a need to synthesise the process using computer modelling to gauge their potential environmental benefits.

In this context, this thesis proposes a systematic framework capable of analysing a region to identify a suitable CCU pathway and then quantify the impacts of its application. This multi-faceted assessment goes from a macro to a micro-scale, shifting the resolution of analysis to accurately quantify its impacts and associated benefits. From a top to bottom exploration, the analysis starts from a global perspective on carbon levels and CCU potential, towards a national assessment closely linked to a sector level, and finally to a plant size with special attention to the process and reaction scale. After quantifying the pertinent impacts at high resolution, the focus is brought back to the initial higher levels to discuss the considerations of the sustainability of its application.

The framework is applied to the case study of the Australian economy to illustrate the methodology. After identifying the optimal sectors of focus and selecting a particular chemical product and CCU pathway, the assessment quantifies the benefits of producing such a chemical via an early-stage technology in a specific region of the country. A sensitivity analysis finally tests the representativeness of the results and the viability of the pathway.

The present research hypothesises that a framework incorporating tailored techno-economic and environmental modelling, process design, and technological considerations can determine the suitability and sustainability of an early-stage CCU system in a delimited economic region.

## 1.1 Research aims

The main objective of this thesis is to provide a systematic methodology that addresses technical, environmental, and socio-economic parameters to be considered for assessing a sustainable CCU application. The proposed framework aims to identify a suitable pathway in a specific region according to socio-economic considerations, quantify its potential environmental impacts at high resolution, and discuss the sustainability of its application.

The specific goals within this research project include reducing the gap of knowledge in CCU pathways, providing a comprehensive review on the existing CCU technologies, the models used to analyse them, and the key associated parameters. The sustainable application of CCU relies first on accurate understanding of all the environmental impacts and energetic requirements associated with it.

Secondly, the methodology created aims to provide a complementary tool for the analysis and selection of CCU technologies, with a special focus on early-stage development. It can give an understanding on the complex configuration of CCU, indicating the relationship with all pertinent parameters and identify areas for improvement. Specific carbon strategies or future research and development can be promoted according to the analysis performed in this framework.

The novelty of the proposed framework resides in the useful integration of methods that are specifically tailored to CCU systems with a low TRL. The model created as a first line of analysis is an innovative extended input-output analysis model

integrated with multi-objective optimisation capable of mapping a scenario of emissions reductions with a minimal effect on the selected socio-economic parameters. Later, an entire system is modelled through simulations and comprehensive process design to include product separation and heat integration. Additionally, the inventory considerations in a life cycle assessment provide a guideline to approach early-stage CCU technologies specifically. Lastly, the case study used to portray the benefits of this framework is unique since the reference used in the comparison assessment is bio-based, which is not the norm in existing CCU guidelines. Because of this new bio-based scenario, some ambiguity in the LCA is identified and overcome.

## 1.2 Outline of thesis

The structure of the thesis mirrors the narrative of the proposed assessment framework, performing a top-down analysis from a global scale to the highly-detailed reaction level. Figure 1.1 illustrates the change of resolution throughout the chapters.

Chapter 2 provides an overview of carbon sources, capture, and CCU from a global perspective, including a literature review on utilisation pathways, examples of large-scale CCU processes, pilot-scale and commercial plants worldwide, and relevant assessments.

After reviewing different opportunities globally, the framework moves towards a national level analysis. Chapter 3 outlines the modelling framework of the extended input-output analysis and multi-objective optimisation model. The case study of the Australian economy starts in this chapter, analysing all industrial sectors of the economy and identifying the key sectors of further focus. Appendix A includes the sector correspondence tables between different sector classifications used in this model.

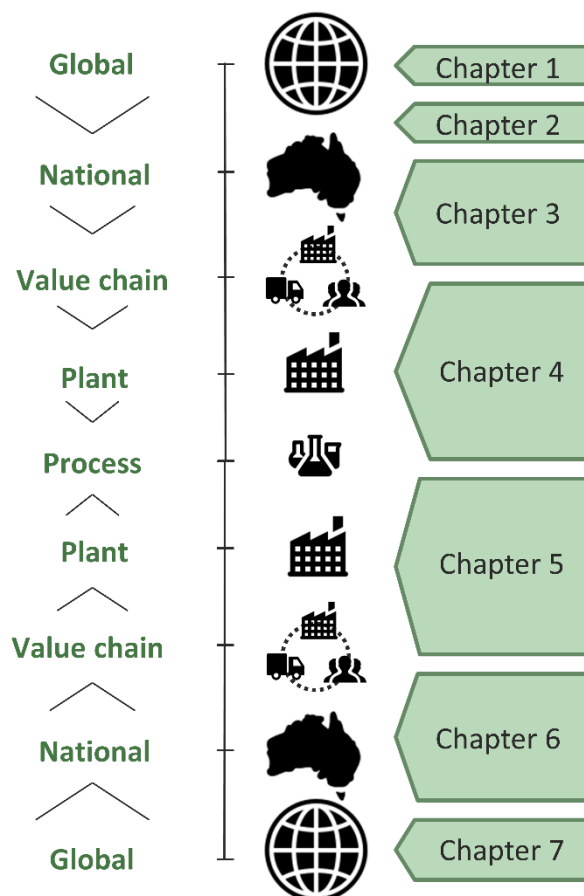


Fig. 1.1 General scope and narrative of research with outline of thesis chapters. *Icons from opensource website icons8.com*

Chapter 4 looks at the relevant value chains to select a process or chemical, and then describes the methodology to develop the life cycle assessment (LCA). First, a specific process and associated CCU pathway is selected according to the overlap of large-scale CO<sub>2</sub> conversion pillars and the associated value-chains of the sectors identified in the previous model. Then, considerations for the methodology of the LCA and the associated process modelling of the proposed system are provided, including considerations when data is not available. Following the case study, the focus is brought to ethanol production with the electrochemical conversion of CO<sub>2</sub> as the CCU pathway. The highest resolution of the analysis is illustrated by the description of the reaction scheme and the process modelling required to design the electrolyser and the novel auxiliary system.

Chapter 5 covers the results of the LCA, outlining general considerations in the results and interpretation of a general assessment before presenting the entire LCA of the case study. The focus is brought back to a plant and regional level, presenting the environmental benefits of producing ethanol through the proposed electrocatalytic captured CO<sub>2</sub> reduction system and compare it with the traditional fermentation of sorghum in Queensland, Australia. Appendix B includes all the detailed associated inventories used in the assessment.

The discussion is continued in Chapter 6, where the different components of the sustainability of the proposed system are discussed. A preliminary economic evaluation determines the magnitude of the capital cost of the proposed system. Then, scenario and sensitivity analyses of the results uncover the environmental uncertainty associated with the assessment. Finally, the discussion includes socio-political considerations and arguments regarding the social perception of CCU. Additional plots of the analysis are included in Appendix B.

Finally, Chapter 7 offers the concluding remarks and recommendations for future work to be taken in continuing the proposed research.

## 2 Literature Review

Carbon capture and utilisation (CCU) presents the benefit of converting recovered CO<sub>2</sub> from a particular source into a valuable product. By only employing carbon capture and storage (CCS), CO<sub>2</sub> can be removed from the atmosphere, but the molecule is sequestered geologically and its intrinsic energy potential is never used. Instead, a multiple array of chemicals can be produced by reusing the captured CO<sub>2</sub>, offering an economic incentive, a fossil fuel substitute, and a vector for surplus renewable energy. However, since CCU involves energy-intensive processes, an analysis needs to be made to determine the real benefits of the entire mechanism. Before presenting the proposed framework, the general mechanism and characteristics of CCU and auxiliary technologies should be comprehended.

This chapter provides an overview of the source and fate of carbon related to CCU. Mentioning different methods for its capture and the comparison with CCS, the narrative of the utilisation part is driven from existing different methods all the way to chemical conversion of CO<sub>2</sub>, which is the main focus of this research. Examples are provided to identify the environmental benefits and challenges of CCU technologies. Additionally, assessment modelling examples are included to show how CCU has been analysed in the past, and their associated methodological considerations. Finally, large-scale pilot and commercial plants using CCU are mentioned to provide a proof of how this technology can already work at present day. The chapter concludes summarising the research gaps identified and the aim of the thesis.

## 2.1 Introduction

Carbon capture and utilisation (CCU) or carbon capture and recycling/re-use (CCR) involves capturing CO<sub>2</sub> from a source, obtaining it in a required concentration, and then using it for a specific purpose. CCU has different pathways and technologies, each with a distinctive method to use CO<sub>2</sub> in a beneficial way. While all share the characteristic of capturing CO<sub>2</sub> to convert or use it in a process, they can be extremely different. All of them have advantages, disadvantages, and a different technology maturity. A detailed analysis of the different stages of CCU is useful to understand the characteristics of its specific processes.

This chapter will provide a review on the source of CO<sub>2</sub>, its capture, the comparison to CCS, different possible conversions, large-scale utilisation processes, and relevant modelling assessments. Finally, a summary distils the main gaps of the review to be filled in the aims of this research. It should be noted that Chapters 3-5 also include a literature review pertinent to the specific topic and framework involved in each level of analysis. This chapter includes a literature review on carbon capture and utilisation as a whole, presenting its key aspects, viable technologies and pertinent methodological considerations to analyse them.

## 2.2 CO<sub>2</sub> sources

The first stage is the source of CO<sub>2</sub>. Emissions from human activities are responsible for the lack of homeostasis in the carbon cycle, making it key to focus on the processes of these activities. Figure 2.1 shows the global CO<sub>2</sub> emissions in 2018 per sector. Power generation continues to be the largest emissions driver in the world (IEA 2020c). The electricity and heat emissions can be reallocated to final sectors, indicating that *industry* (manufacturing industries and construction) was the largest polluting sector with over 36% of all global emissions.

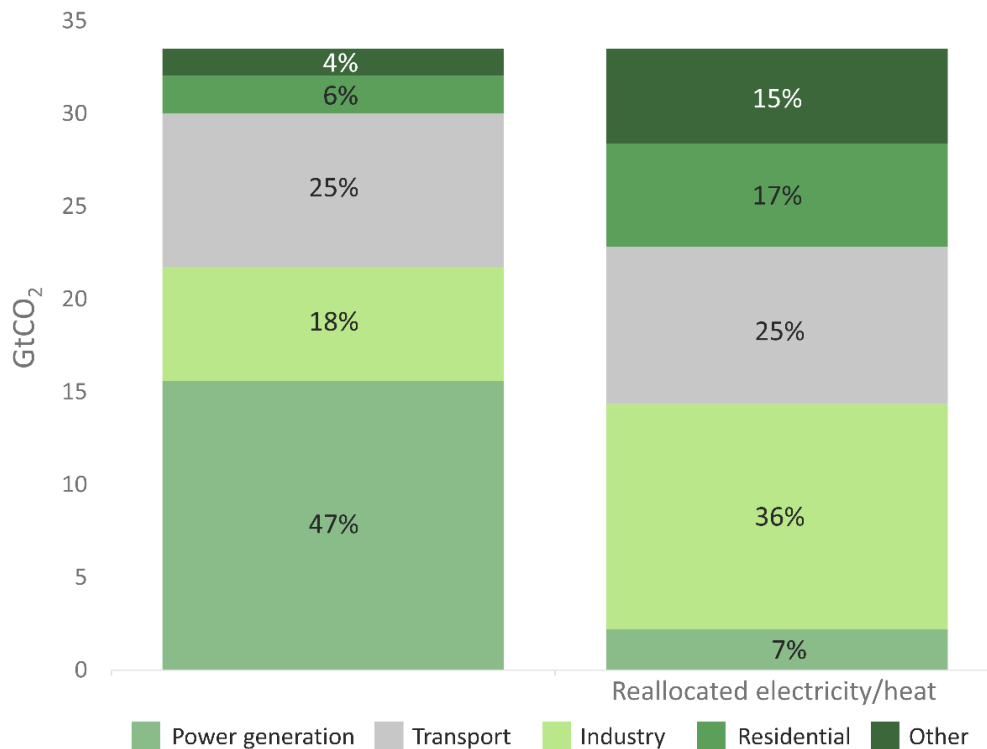


Fig. 2.1 Global CO<sub>2</sub> emissions by sector in 2018. 'Other' includes commercial and public services, agriculture/forestry, fishing and non-specified final energy consumption. Bar plot on the right reallocates the electricity and heat of Power generation to the sector where it is ultimately consumed. Data from IEA (2020c)

The potential magnitude of CO<sub>2</sub> utilisation is a function of the demand of products manufactured by CCU. The level of carbon mitigation has been estimated to be 1.5 Gt CO<sub>2</sub> in chemical manufacturing (Centi & Perathoner 2011) and up to 7 Gt CO<sub>2</sub> per year, considering other industry areas and the implementation of auxiliary strategies (Global CO<sub>2</sub> Initiative & CO<sub>2</sub> Sciences Inc. 2016). However, when this amount is compared to the global CO<sub>2</sub> emissions (~34 Gt CO<sub>2</sub> per year) there seems to be a substantial mismatch.

Nonetheless, CCU presents a potential for success. The synthetic carbon cycle that can be achieved through CCU is of a much shorter span (Styring et al. 2015b) and addresses the smaller fraction of the global cycle that cannot be processed naturally (Aresta 2010). Moreover, the production of chemicals with market value from 'waste' streams provide economic incentives that can motivate the paradigm shift of existing



and new processes to introduce CCU (Quadrelli et al. 2011). Specifically in the chemical industry, a major driver for CCU is substituting waste CO<sub>2</sub> for fossil resources as feedstock (Kondratenko et al. 2013). Finally, the incorporation of other industries with lower investment costs and the enactment of carbon tax policies can increase CCU demand to substantial magnitudes (Rafiee et al. 2018).

## 2.3 Carbon capture technologies

Because of the high level of emissions responsibility, a substantial industrial effort has been put to the development of techniques that capture CO<sub>2</sub> from the combustion of fossil fuels. There are four main approaches for carbon capture, categorised according to the nature of the combustion: pre-combustion, oxy-fuel combustion, post-combustion, and chemical looping. This section only offers a brief background and overview; it does not intend to provide a full description of these technologies. Cuéllar-Franca and Azapagic (2015), Sifat and Haseli (2019), and Osman *et al.* (2020) provide a comprehensive and complete account of these and the current state of the art.

Although there has been much development in pre-combustion (Cao et al. 2020; Petrakopoulou & Tsatsaronis 2012; Zhai & Rubin 2018) and interest in oxyfuel combustion capture (Portillo et al. 2019; Wall & Stanger 2011; Wienchol et al. 2020), the most mature approach is post-combustion capture (PCC) because of the accessibility of applying this mechanism to already existing industrial plants (Deutch & Moniz 2009).

Commercial development for PCC had a boost in the 1970's (Herzog et al. 1997), where the recovered CO<sub>2</sub> would be used for enhanced oil recovery (EOR) operations (St Clair & Simister 1983). Those early stages used amine-based solvents like monoethanolamine (MEA) (Arnold et al. 1982), therefore establishing solvent-based absorption-desorption capture technologies as the most widespread (Styring 2015a).

A number of studies have modelled and optimised solvent-based PCC technologies for specific plant conditions (R. Khalilpour 2014; Z. Li et al. 2013), with some of them concluding that the heat necessary for regenerating the solvent has the highest impact (Oexmann et al. 2012), falling into a considerable energy penalty (R. Khalilpour & Abbas 2011). However different PCC technologies have been explored through membranes (Khalilpour et al. 2015), adsorption (Ho et al. 2008; Wang et al. 2011), and solid sorbents (Wang et al. 2014). Next-generation prospective PCC technologies include ionic liquids (Supasitmongkol & Styring 2010), metal organic frameworks (Ding et al. 2019; Y. Liu et al. 2012), enzymatic membranes (Pierre 2012), and biological processes (Zhao et al. 2013).

Calcium looping is an attractive route for PCC, although it may also be used in pre-combustion capture (Bui et al. 2018). The CO<sub>2</sub> is exothermically captured and then released through calcination in a reactor employing generally coal or natural gas (Adams et al. 2017). However, the heat produced reduces considerably the energy requirements of conventional PCC (Hanak & Manovic 2016).

An emerging and promising technology is chemical looping combustion. It is based on a similar mechanism as oxy-fuel combustion, except the oxygen required is supplied through metal oxides (Cao et al. 2006). It has been regarded as one of the cheapest and least energy-intensive capture technologies (Adanez et al. 2012). However, as Markewitz *et al.* (2012) concluded, development is still needed to explore these new frontiers and reduce the efficiency losses and investment costs of existing technologies.

The specific source of CO<sub>2</sub> will also have an effect on the required technology and associated energy to capture it. While power generation is the highest emitting sector, the concentration in flue gas is low. Table 2.1 shows the average range of CO<sub>2</sub> concentration in several streams of different sources. The production of steel and cement have great potential for decarbonisation that is yet to be fulfilled (Cuéllar-Franca & Azapagic 2015). One very important interest in carbon capture is removing

CO<sub>2</sub> directly from the atmosphere or through direct air capture (DAC). Although the concentration of CO<sub>2</sub> is substantially lower, DAC has the capacity to reduce CO<sub>2</sub> emissions that are difficult to capture from the source -such as in the transport sector (Styring 2015a). Advances in PCC technologies have been instrumental in developing viable DAC systems (Keith et al. 2018). Highly pure CO<sub>2</sub> from fermentation will be discussed in later chapters.

Table 2.1 CO<sub>2</sub> concentration in volume from streams of various sources prior to capture. Data from IPCC (2005), Styring (2015), and IEA (2019). SMR = steam methane reforming

Source	CO <sub>2</sub> concentration
Coal power generation	10-15%
Natural gas power generation	3-10%
Ammonia production	18%
Ethylene oxide	12%
Hydrogen production (SMR)	15-20%
Steel production	21-27%
Cement production	20-30%
Fermentation	~100%
Atmosphere	0.04%

### 2.3.1 Carbon capture and storage

Carbon capture and storage (CCS) or sequestration aims to capture CO<sub>2</sub> and store it in underground geological reservoirs (Metz et al. 2005). The main types of storage sites are saline aquifers, depleted oil and gas reservoirs, and not mineable coal seams (Aydin et al. 2010). However, this technology would only be sustainable if the reservoir is able to permanently store the injected CO<sub>2</sub>, and that has not been confirmed for most of the potential sites (Folger 2018).

CCS involves high costs, both economically and energetically. Only in places where there are substantial state subsidies or revenue from enhanced oil recovery

(EOR) does CCS appear to be viable (Baxter 2017). Currently, the largest capacity CCS plants in the world -Shute Creek, Century Plant, and Petrobras Santos- capture CO<sub>2</sub> from natural gas processing and reinject it into oil fields for EOR (Global CCS Institute 2020).

The sole remaining fossil fuel-powered plant in the world that employs CCS at a large-scale is the Boundary Dam plant in Saskatchewan, Canada (MIT 2016). The only other recent example, the Petra Nova plant in Texas, shut down in May 2020 because of low oil prices (Groom 2020). Both of them captured CO<sub>2</sub> via PCC to sell a fraction of it for EOR and store the rest in underground basins.

It can be seen that, even though CCS has a substantial presence in current portfolios for reducing emissions globally and heavy investment stimuli have been put forward, its deployment continues to be underdeveloped (IEA 2020b). The associated high capital and operating costs, cross-chain risks, and public acceptance (Booth-Handford et al. 2014) has made CCS lose its momentum for large-scale deployment.

Geological sequestration seems to only offer a partial solution since it cannot cope with the amount of CO<sub>2</sub> that needs to be eventually reduced, it is endemic to particular regions (Cuéllar-Franca & Azapagic 2015), and could even be perceived as a temporary solution with potential delayed release (Aresta 1999). Additionally, disposing CO<sub>2</sub> without any value creation represents an inherent economic and energetic loss (Dechema & VCI 2009). When the perspective of CO<sub>2</sub> is shifted from being a waste towards being a feedstock and chemical commodity, the useful pathways of carbon capture and utilisation (CCU) are uncovered. By further including a utilisation component, costs for transport can be reduced and economically valuable products or services are obtained from it (Quadrelli et al. 2011).

## 2.4 Carbon utilisation pathways

CO<sub>2</sub> utilisation can be primarily divided into physical and chemical uses. Physical pathways utilise CO<sub>2</sub> but it remains chemically unchanged throughout the process. Some areas of interest include the food industry (Brunner 2005), textiles (Ahmed & El-Shishtawy 2010), refrigerants (Goetzler et al. 2013), enhancement of oil and gas recovery (Khan et al. 2013; Narinesingh & Alexander 2014), among many others (Licence et al. 2003).

Liquid and supercritical CO<sub>2</sub> play a considerable role in the field of solvents, as they are commonly used as extraction solvents (Moyler 1993). CO<sub>2</sub> is suitable for natural extractions because of its non-toxicity and tasteless properties (Atti-Santos et al. 2005). It is also considered a greener alternative because of its high recovery rate after use (Marriott et al. 2015). Also, its solvent properties can be manipulated by pressure and temperature conditions (Ikushima et al. 1991), to the point of creating CO<sub>2</sub>-expanded liquids (Jessop & Subramaniam 2007) and switchable solvents (Jessop et al. 2012) which offer a further variety of customisation for industrial applications (Ramsey et al. 2009).

Notwithstanding the considerable benefit of the joint application of all these physical pathways, CO<sub>2</sub> is not being transformed and the carbon demand from these markets alone would not have a substantial effect on global CO<sub>2</sub> reduction (Muradov 2014). As Rafiee *et al.* (2018) succinctly concluded, physical pathways are mature but have a limited demand that can only offer an opportunity for growth through policies and market dynamics. Specifically for EOR, although there is economic incentive and carbon abatement potential, it does not solve the depletion of fossil resources and the dependence on their continued combustion. Chemical pathways instead present a potentially high demand for a variety of increasing applications that offer a substitute

for fossil resources. Therefore, the focus of this research is on the chemical transformation of CO<sub>2</sub>.

### 2.4.1 Chemical uses of CO<sub>2</sub>

Chemical pathways have CO<sub>2</sub> directly or indirectly transformed, operating in the synthesis of a product or in enhancing the process (Huang & Tan 2014). Despite the low reactivity and relative inertness of the CO<sub>2</sub> molecule (North 2015), there is a vast and eclectic panorama for chemical uses. As Styring *et al.* (2011) categorise, three main areas of focus can be discerned: carbon mineralisation, enhanced biological conversion, and conversion as chemical feedstock.

Carbon mineralisation involves chemically transforming minerals –most commonly calcium and magnesium based– and alkaline industrial wastes into stable solid carbonates, in an effort to deposit large quantities of CO<sub>2</sub> into long life-time products (Gadikota & Park 2014). Mineralisation is thermodynamically favoured and offers an alternative to locations where geological storage is infeasible (Aresta *et al.* 2014). Therefore, this area has more affinity to CCS, since it stores CO<sub>2</sub> in long period sinks. However, its products can also be employed in the building industry (Jang *et al.* 2016), which has potential for large demand.

Enhanced biological conversion involves mostly the use of algae or microorganisms with synthetic systems to transform CO<sub>2</sub> through photosynthesis. Photobioreactor ponds with algae can have large CO<sub>2</sub> fixation from flue gas of power plants, giving a high biomass productivity per unit area (Pulz 2001), and a number of other valuable products (Faried *et al.* 2017). Some of the disadvantages include operational complexity, high investment, maintenance costs, and land use (Collotta *et al.* 2018).

Finally, conversion of CO<sub>2</sub> as chemical feedstock is a broad field that provides an extensive array of possibilities. The first known chemical pathways of CCU as

chemical feedstock are the synthesis of salicylic acid (1869), the Solvay process (1882), and the conversion of ammonia and CO<sub>2</sub> into urea (1922), making those industries very mature nowadays (Aresta 2006). Currently, the horizon on chemical conversions involves many feasible end products or building blocks for further synthesis through carboxylation or reduction. However, not all reactions schemes can be applied in large-scale, which is the focus of the proposed research.

## 2.5 Potential large-scale areas of utilisation

Potential large-scale conversion routes can be clustered into four pillars: mineralisation, biochemical or biological conversion, organic carboxylation, and reduction to hydrocarbons and fuels (Quadrelli et al. 2011). The suitability of these areas comes from their economic viability, their potential to leverage existing infrastructure, and the involvement of relatively simple reactions (Armstrong 2015). The first two pillars have already been discussed in the previous subsection.

Organic carboxylation features in the field of production of organic carbonates, including linear carbonates from alcohols (Fan et al. 2009), cyclic carbonates from epoxides (Dai et al. 2009), and carboxylation of alkenes (Omae 2012), with some research focusing on innovative catalysts (Ang et al. 2015; Chang et al. 2018). Urea synthesis has the largest volume of industrial use of CO<sub>2</sub> (Alper & Yuksel Orhan 2017), and it is used worldwide for fertilizers, polymer synthesis, and nitrogen-based applications for engines (Maxwell 2012). Integrated systems, such as the one described by Ishaq *et al.* (2021) have been developed to produce urea directly with captured CO<sub>2</sub>. Other organic carbonates also have a considerable market size with potential to increase (Aresta et al. 2016).

The last pillar comprises reduction reactions to hydrocarbons and fuels, which involve the reaction of CO<sub>2</sub> with reducing agents like hydrogen, methane, and electrons

(Quadrelli et al. 2011). Some of the most important chemicals in this area are methanol, ethanol, formic acid, dimethyl ether (DME), methane, and syngas (CO/H<sub>2</sub>). More recently, the Global roadmap by the Global CO<sub>2</sub> Initiative and CO<sub>2</sub> Sciences Inc. (2016) confirmed that the processes with the highest economic and carbon mitigation potential are accelerated mineralisation and synthetic fuel production. The advantages of synthetic hydrocarbons are numerous, since they can act as fuels or as building blocks for a variety of chemicals (Dowson & Styring 2014).

Otto *et al.* (2015) developed an exhaustive compendium of over 120 CO<sub>2</sub> conversion paths, evaluating and categorising the chemicals synthesised into fine and bulk chemicals. Their results for bulk chemicals indicated that the production of methanol, dimethyl ether (DME), formaldehyde, and formic acid had the most potential. One of the most important factors in their criteria was the capability to produce large volumes of simple products that are commonly manufactured through fossil fuels. Therefore, not only can these chemicals function as alternative chemicals and fuels, but also as drivers to displace the reliance on fossil fuels.

### 2.5.1 Conversion to synthetic hydrocarbons and fuels

Synthetic hydrocarbon production presents a substantial potential for CCU. For example, methanol production is considered to be mature and versatile, since it opens a wide range of applications and products. Olah *et al.* (2009a) greatly contributed to the proposal of a cyclic ‘methanol economy’ from CCU, in which this molecule could be used as fuel or fuel additive and as a building block for chemicals like olefins, DME, acetic acid, syngas, formaldehyde, and even gasoline. Olah (2013) suggests that methanol can function as a replacement for oil as raw material for derived industrial products, boosted by price fluctuations and diminishing oil reserves.

Higher alcohols, such as ethanol (Kusama et al. 1996), are also attracting attention as fuel alternatives (Surisetty et al. 2011) and as feedstock for further



synthesis (Sun & Wang 2014). They have the advantage against methanol of being less toxic and easier to transport (Nieskens et al. 2011). DME, with a cleaner combustion than conventional diesel (Coates & Moore n.d.), is in part capable of replacing it (Semelsberger et al. 2006), as well as liquefied petroleum gas (LPG), compressed natural gas (CNG), and liquefied natural gas (LNG) in several applications (Olah 2013). A transition to a synthetic alcohol economy would increase CO<sub>2</sub> utilisation levels considerably (Thybaud & Lebain 2010).

Currently, by an economic point of view, the hydrogenation of CO<sub>2</sub> (Jadhav et al. 2014) is the most promising reaction scheme for low-chain oxygenated hydrocarbons (Leonzio 2018), although hydrogenation of syngas, commonly known as gas-to-liquids (GTL), is the most common industrial technique (Olah 2013). Co-electrolysis of water and CO<sub>2</sub> (Al-Kalbani et al. 2016), photocatalytic (Jia et al. 2019; Sakimoto et al. 2017), electrocatalytic reactions (Malik et al. 2017; Zhang et al. 2019), and other different innovative approaches (Bozzano & Manenti 2016) are emerging as feasible alternatives.

CO<sub>2</sub> is a highly stable molecule, so it requires significant amounts of energy per unit mass to react chemically towards other products even in the presence of efficient catalysts (North 2015). Therefore, with the exception of mineralisation technologies, CCU processes are energy-intensive (Styring et al. 2015a). To avoid creating more emissions than the offset acquired through the capture, this energy would need to come from clean or renewable sources.

## 2.6 Renewable energy

The inclusion of renewable energy into CCU can avoid incurring more emissions or environmental impacts than those associated with the emissions prevented (Schakel et al. 2016). This energy is integrated to power the entire system and specifically boost

the reactivity of CO<sub>2</sub>, being very thermodynamically stable in reduction reactions (Gibson 1996).

The integration of renewable energy can happen during the capture process, as in Qadir *et al.* (2015), where the operation of a solvent-based PCC plant is assisted with a dynamic input of solar thermal energy, incurring a reduction on emissions and revenue loss. Alternatively, the hybridisation with renewables can happen on the conversion itself. Solar energy, in Du *et al.* (2015), participates in the catalytic conversion of propane, or in Masel *et al.* (2014), is introduced to power the electrolyzers that convert CO<sub>2</sub> in a series of reactions to formic acid, formaldehyde, and other chemicals with high conversion rates.

Biomass can also be used, as in Sharifzadeh *et al.* (2015) where captured CO<sub>2</sub> during biomass pyrolysis can produce microalgae with improved conversion. In the field of oxygenated carbonates, methanol can be produced through solar energy in the SOLME process (von Storch *et al.* 2016), through gasification of solid wastes (Iaquaniello *et al.* 2017), through switchgrass (Martín & Grossmann 2017), and many other innovative renewable sources (Shamsul *et al.* 2014).

The benefits of using renewable energy in CCU can be bilateral, as surplus energy from renewable sources can be chemically stored and transported through the manufactured products. CCU pathways can convert and store energy from renewable sources in chemical form. Given this quality of facilitating storage and transport, CCU pathways are able to function as renewable energy vectors (Artz *et al.* 2018).

The recovery of the stored energy is available in many forms. There are studies that focus on storing excess renewable energy with liquid CO<sub>2</sub>, recovering energy when required by oxidising the molecule, and afterwards recovering it and liquefying it again for storage (Al-musleh *et al.* 2014). Alternatively, the incorporation of solar energy to the production of synthetic hydrocarbons can establish them as well as solar fuels, useful for both storage and transportation (Centi & Perathoner 2010).

The use of these low-chain hydrocarbons could present a cheaper and simpler alternative (Quadrelli et al. 2011). For example, synthetic fuel storage allows the use of existing chemical infrastructure, which can lead to benefits on capital investment and long duration storage (Hall et al. 2015). Integrations of renewable energy with CCU, such as those proposed by Centi *et al.* (2013) and by Olah *et al.* (2009b), introduce a sustainable economy that relies on chemicals production and storage. Developments in catalysts and other conversion techniques keep opening opportunities in the field of fuel production (Zhou et al. 2019).

The efficiency of the conversion of surplus electrical energy to chemical energy needs to be considered to avoid energy wastage. As analyses of early-stage CCU technologies do not usually include auxiliary processes and product separation, the energy efficiency may be overstated. Therefore, the assessment of the complete CCU system is necessary to offer an accurate perspective on their potential for acting as a renewable energy vector.

In summary, particular CCU pathways present not only the benefits of reducing emissions and producing profitable chemicals, but can also serve as fossil fuel substitutes and renewable energy vectors. CCU then has an inherent potential to reduce emissions directly and indirectly while decreasing fossil resources depletion (Centi et al. 2013). However, to properly identify the real benefits of these technologies, comprehensive analyses of the environmental impacts should be assessed from a life cycle perspective (Hellweg & Canals 2014).

## 2.7 Life cycle assessment

Life cycle assessment (LCA) is a standard methodology able to evaluate the energy and environmental footprint of the various stages in the life cycle of a specific product or process, ensuring all relevant flows are included in the analysis (ISO 2006a). Chapter

4 provides a detailed background on the definition of LCA and its specific application to CCU. This section only provides a brief overview of the methodological approaches and present gaps in the literature.

LCA provides an objective quantification of the environmental burdens to take an informed decision between available technologies (Dechema & VCI 2009). Specifically for CCU, LCA can provide the means to estimate the full environmental impact of CCU technologies avoiding a singular focus on just global warming. It ensures that impacts are not just transferred to another process outside of the analysed system's borders. A cradle to grave approach may also indicate key sections on the complete structural path of CO<sub>2</sub>. As Müller and Arlt (2014) argue, the supply of the reactants and the energy demand of the process can have more effect than the amount of CO<sub>2</sub> produced in the reaction itself.

### 2.7.1 Methodological guidelines

Although the practice of LCA in general is standardised, guidelines on conducting such an assessment for the specific characteristics of CCU were not available until relatively recently. While initial efforts were made from several groups such as von der Assen *et al.* (2014), the nature of conducting LCA for CCU was primarily *ad hoc*. Results would vary significantly according to the assumptions made by the researcher, especially when assessing emerging technologies (Sathre et al. 2012).

One of the earliest specific applications of LCA for CCU was done in 1996, when Bertilsson and Karlsson (1996) proposed a framework to estimate total CO<sub>2</sub> emissions from CCU, trying to divert from over-simplistic economic and technical criteria -such as product lifetime- that also disregard environmental impacts. The purpose of their study was to employ analyses that ensured less emissions through the substitute product, focusing on several common life-cycle practices. CCS normally assesses the period between capture and eventual release as a paramount factor (Metz et al. 2005).

However, the lifetime of the product in CCU does not necessarily share the same importance, with the exception of production of polymers and other carbon-integrated products of long duration (Langanke et al. 2015), because CCU products can indirectly replace fossil fuels and become energy vectors of renewable energy sources.

A number of different LCA studies focused solely on the carbon footprint of the process. For example, Dominguez-Ramos *et al.* (2015) formulated a comprehensive LCA for the electrochemical reduction of CO<sub>2</sub> to formate-based products in order to assess its environmental sustainability. However, this study is limited to greenhouse gas (GHG) emissions, which only gives a partial environmental point of view. Artz *et al.* (2018) stressed the importance of not considering global warming potential as a sole metric. After reviewing LCAs for the production of a wide range of chemicals and identifying a trend of only reporting global warming or energy balances, the authors concluded future assessments should provide a comprehensive range of all relevant environmental impacts.

Because of the lack of a coherent guideline for goal and scope definition in an LCA, the comparison of results has been ineffective. Cuéllar-Franca and Azapagic (2015) analysed sixteen LCAs for various CCU applications and identified that many studies employ different functional units or system boundaries in their assessment. Therefore, time-consuming studies such as this need to be developed to recalculate results and harmonise the inconsistent assessments to provide a fair comparison between them (Cuéllar Franca & Azapagic 2017).

A more recent example is found in the LCA on power-to-gas (P2G) by Zhang *et al.* (2017), where a different approach to system expansion or subdivision in the system boundaries would create differing results. Additionally, since P2G may also be considered as a long-term energy storage pathway, the authors acknowledged their study was only a partial approach since the technology should also be compared against

other large-scale seasonal storage pathways such as pumped hydro and compressed air energy storage.

In 2018, The Global CO<sub>2</sub> Initiative released the first iteration of the techno-economic and LCA guidelines for CCU, detailing a comprehensive set of recommendations to conduct an assessment in a coherent and reproduceable way (Zimmerman et al. 2018). These guidelines set the standard for LCA application to CCU, considering the difficulties with goal and scope, carbon accounting, recommended impact categories, and other assumptions. The second version was released more recently, with updated aspects and more concise recommendations (Zimmermann et al. 2020). Although one of the most comprehensive and universal, these are not the only guidelines. Other reports offer guidance for single impacts (IEAGHG 2018), special types of products (Edge Environment & Lifecycles 2016), or conditions specific to a country (Skone et al. 2019).

Notwithstanding the existence of helpful guidelines such as these, there are still discrepancies in the reported impacts of different studies. Müller *et al.* (2020) concluded that this is a consequence of the persistent methodological ambiguity in solving the multifunctionality of CCU pathways. Moreover, different components relevant to the CCU system may have a substantial effect on the assessment.

## 2.8 Additional considerations in CCU assessments

An energetic co-reactant, such as hydrogen, is usually needed in catalytic CO<sub>2</sub> conversion (Klankermayer & Leitner 2016). In terms of the production of synthetic hydrocarbons, Aresta *et al.* (2002) conducted an LCA on the production of methanol through four different synthesis routes: three through syngas from different configurations of dry and steam reforming, and one of hydrogenation of CO<sub>2</sub> with hydrogen from either photovoltaic (PV) or nuclear energy. Their conclusion is the

hydrogenation with hydrogen sourced from PV is the most effective route in terms of both energy and environmental criteria.

However, Utgikar and Thiesen (2006) analysed the production methods for hydrogen through a mix of different renewable energies, concluding that wind energy contributed the least for emissions impact, approximately two times less than solar thermal and four times less than solar PV. It is noteworthy to mention that nuclear energy resulted in a reduced carbon footprint but had a substantial increase in magnitude from other impacts. The differing conclusions from these previous studies demonstrates that, with increasing development of new technologies and cheaper renewable approaches, LCA studies need to be revisited and reproduced to draw reliable conclusions.

Only a few assessments have focused on the importance of the specific location of the CO<sub>2</sub>. One example is found in von der Assen *et al.* (2016), where the authors introduced an environmental-merit-order curve as a tool to prioritise CO<sub>2</sub> sources to minimise GHG emissions and fossil fuel depletion through CO<sub>2</sub> supply. Their LCA considered CO<sub>2</sub> sources in Europe and matching them to optimal sinks, referred to as CO<sub>2</sub> “oases” for supply. Their results show that capture presents more GHG reduction against the reference, but its magnitude is completely dependent on the source, favouring capture from chemical production and natural gas processing. Hoppe *et al.* (2018) corroborated the importance of the CO<sub>2</sub> source in the sustainability of the production of methane, methanol and syngas with CO<sub>2</sub> from different sources using wind power for the hydrogen production, favouring CO<sub>2</sub> from cement kilns or waste incineration.

The integration of all required flows within the CCU system is critical to create a more reliable assessment. Pérez-Fortes *et al.* (2016) produced an assessment on the production of methanol to observe the net reduction of CO<sub>2</sub> compared to conventional European processes. Their results indicated that there was only a marginal reduction

on CO<sub>2</sub> emissions. However, they considered CO<sub>2</sub> and hydrogen as external flows, which would differ if the model had integrated the plants that have those raw materials as ‘waste’ products.

Only a few assessments focus on geographical conditions explicitly and examine the suitability of regions to undertake a particular CCU pathway. Sternberg *et al.* (2017) ranked the production of formic acid, carbon monoxide, methanol, and methane via a one-step catalytic conversion in a comparative LCA. The study analysed the suitability of European countries to produce these chemicals by using each country’s national electricity mix to power the electrolysis for hydrogen production. Formic acid production through CCU was determined to have the highest environmental impact reductions on global warming and fossil resource depletion, followed by methanol, carbon monoxide, and methane.

The integration of optimisation techniques with a geographical focus is also powerful. Hasan *et al.* (2015) developed a framework for CCU coupled with geological storage for the US. This framework has a multi-scale design that covers the CO<sub>2</sub> flow from the source to the utilisation process and finally to the sequestration site. Their network reduces up to 50% of stationary emissions in the US. However, utilisation in this framework is only focused on EOR. The incorporation of chemical pathways for the utilisation step would substantially complement this approach.

Similarly, Mohd Nawi *et al.* (2016) created a ‘Total Site CO<sub>2</sub> Integration’ that used pinch analysis to maximise the utilisation of CO<sub>2</sub> before it is geologically stored. The model allocated the required amount of CO<sub>2</sub> with necessary purity to a site with demand for utilisation, optimising the path through pipelines from sources to sink before resorting to CCS. While this method is helpful, it is a numerical method without detailed energy and technical considerations. There is still need to adapt this kind of approaches to a framework that incorporates those essential components plus environmental impacts to be able to produce a robust optimisation.



Unfortunately, data may not be sufficient when the CCU technology assessed is at early stage. Rickman *et al.* (2013) developed a techno-economic and life-cycle analysis to assess if the installation of an algal pond beside a coal plant would be feasible to reduce CO<sub>2</sub> levels. However, the lack of consistent design parameters of the process from other sources led to uncertain conclusions. Therefore, pertinent modelling is required to create missing data and incorporate them in a comprehensive design and model. Technical considerations in assessments are extremely useful to identify benefits in the design of the system. Fernández-Dacosta *et al.* (2018) proved the order of reaction towards DME and polyols had little effect whether done in cascade or parallel, preventing the added effort of recycling CO<sub>2</sub> in the cascade configuration. Modelling provides a means to locate key components and optimise the system, ensuring that the process remains feasible.

Finally, as von der Assen *et al.* (2014) concluded, the importance of comprehensive and accurate environmental assessments resides not only in the understanding of the entire impacts of CCU, but also in the understandable communication of these to an audience who are not necessarily experts in the subject. These studies can accurately generate simple and comprehensible values to be used to build a social acceptance and support for CCU.

## 2.9 Functional commercial or pilot-scale plants

There are already a number of projects and functional plants at pilot or commercial scale operating with CCU. In the pillar of synthetic fuels, Carbon Recycling International (CRI) is the only company that is currently producing liquid fuel at industrial scale (Carbon Recycling International n.d.). The “George Olah Renewable Methanol Plant” from CRI recycles 5.5 kt CO<sub>2</sub> per year, producing more than 5 million litres of renewable methanol sold as “Vulcanol” as a fuel additive and for other

applications. A fleet of methanol-powered cars has already been tested, presenting more than 70% reduction in CO<sub>2</sub> emissions compared to cars with traditional fossil fuels (CRI 2017). The plant uses hydrogen from electrolysis powered by economic geothermal power to produce syngas which is subsequently converted into methanol, establishing the basis of their proprietary Emissions-to-Liquids (ETL) technology.

CRI and a related group of industrial companies and research institutions, under the project FreSMe (FreSMe n.d.), implemented their ETL technology in the steel manufacturing plant Swerea MEFOS in Sweden. It separates CO<sub>2</sub> from blast furnace gas and produce methanol to be used by a Swedish ferry operator. This was facilitated through the MefCO<sub>2</sub> project (MefCO<sub>2</sub> n.d.), which was a joint project from companies of different countries in Europe to confirm the feasibility of using intermittent renewable energy for methanol production and its further applications. CRI is now designing a new facility in the Henan Province in China, using CO<sub>2</sub> from a coke oven gas production plant. It is expected to start commissioning in late 2021, becoming the largest low-carbon methanol production plant in the world, consuming 150kt CO<sub>2</sub> per year (CRI n.d.)

In 2009, Mitsui Chemicals Inc. tested the hydrogenation of CO<sub>2</sub> to produce methanol in a pilot plant (which uses captured CO<sub>2</sub> from the petrochemical plant on site, hydrogen from photolysis, and a highly effective electrocatalyser) with a production rate of 100 tonnes of methanol per year intended for the production of olefins and aromatics (Mitsui Chemicals 2008). This has not been commercialised yet due to costs and availability of hydrogen (Mitsui Chemicals n.d.).

LanzaTech Inc. is a rapidly growing company that produces ethanol, jet fuel, and other chemicals through microbial gas fermentation (LanzaTech 2017). Their technology has been demonstrated at five steel plants and one municipal solid waste plant. One of them in China is already operating commercially, while other plants are proposed for India, South Africa, California, and Belgium (BASF Venture Capital

GmbH n.d.). A commercial flight in 2018 by Virgin Atlantic used LanzaTech's jet fuel to power the entire flight, setting the precedent for low-emissions air transport (Branson 2018).

Lastly, the Kopernikus Project P2X at Karlsruhe Institute of Technology in association with companies Sunfire, Climeworks, and Ineratec is a pilot test facility that started operations in 2019 to produce gasoline, diesel and kerosene from CO<sub>2</sub>. It first captures CO<sub>2</sub> by DAC, then produces syngas by electrolysis, and then produces the hydrocarbons by Fischer-Tropsch (Landgraf 2019). It currently produces 10L of fuel per day, but will increase to 200L in the second phase of the project and to 1500-2000L in a pre-industrial demonstration plant (Sunfire 2019).

In terms of other chemicals, Mantra Energy Alternatives Ltd. developed a novel technology based on the electroreduction of CO<sub>2</sub> (Oloman & Li 2008), which is able to produce formic acid, formate salts, and other chemicals from water and captured CO<sub>2</sub>. A pilot plant was constructed in the LaFarge cement plant in Canada to use flue gas from the cement plant with a rate of 100 kg CO<sub>2</sub> recycled per day (Mantra Venture Group Ltd 2014). More recently, Dioxide Materials has manufactured a commercial electrochemical cell to produce formic acid, underpinning the successful performance of their trademark *Sustainion* anion exchange membrane and ionomer (Dioxide Materials n.d.).

Korea Gas Corporation (KOGAS) were the first to develop a commercially viable one step process for the production of DME, employing a tri-reforming process (Cho et al. 2009). In 2009, the demonstration plant was producing 10 tonnes DME per day, but the target was set on a production of 3 kt DME per day to be used as fuel for industry and machinery and eventually for commercial vehicles and domestic use (Cho 2010).

There are many other examples involving other pathways, such as CarbonCure Technologies (CarbonCure Technologies 2020) and Solidia Technologies (Solidia

Technologies n.d.) for concrete curing, Calix Limited (Calix Limited n.d.) for capture in calcination, Covestro for polyurethanes (Chang 2016), Calera and Skyonic (*Calera* n.d.) and New Sky Energy (*New Sky Energy* n.d.) for inorganic carbonates, Novomer Inc. for polymers (*Novomer* n.d.), and Carbon8 Systems Ltd for carbonated waste (*Carbon8* n.d.).

Based on these examples it can be concluded that CCU is completely feasible to be fitted into an existing plant or to be used as the centre pillar for future designs. However, better economics and increased demonstration is still desirable to the industry. Development in environmental assessments and reliable forecasts from modelling will further encourage the widespread use and knowledge of CCU pathways.

## 2.10 Conclusions

In summary, appropriate implementation of CCU is an industrial solution that tackles multiple fronts. In terms of environment, it can reduce CO<sub>2</sub> emissions and control other impacts; in energy, it can function as chemical storage and transport of energy, especially from renewable sources; in resources, it has the potential to reduce the dependence on fossil fuels for the production of chemicals; and in economic terms, it creates products with market value, which will incentivise its demand and ulterior beneficial impact.

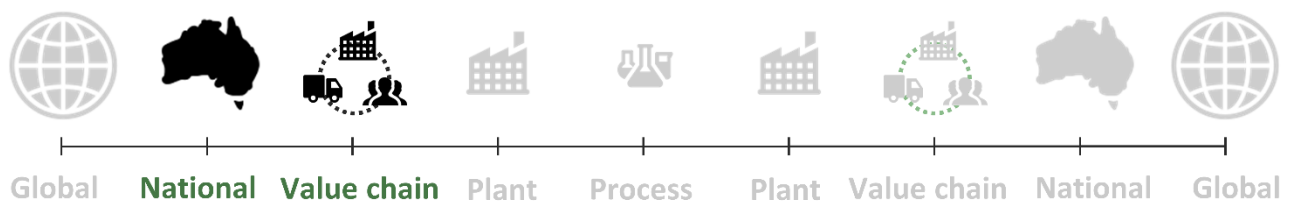
The large-scale CO<sub>2</sub> conversion pillars identified involve mineralisation, biochemical or biological conversion, organic carboxylation, and reduction to hydrocarbons and fuels. Regarding the first and last pillars, there are already a number of demonstration and commercial plants using different CCU pathways. Hydrocarbons and fuels have an especially great potential since they have a vast market, are suitable for energy transportation and storage, and can be used as building block for other chemicals with market value. While CCU can be energy-intensive, the potential of

solving the depletion of fossil fuel resources while still offering a secure supply of chemicals and energy storage is able to motivate its global use (Styring et al. 2011).

Many assessments provide detailed analyses of individual technology performance, but are not necessarily capable of providing a complete framework for decision-making that incorporates other pertinent parameters (Sathre et al. 2012). To help in such decisions, more and more complementary methodologies are used, such as economic analyses, scenario forecasting, and input-output analysis (Weidema 2011). However, there is no single systematic framework that identifies a suitable CCU pathway for a specific region according to its socio-economic and environmental characteristics. As Pekdemir (2015) concluded, the extent of CCU globally and knowing which CCU technology to focus on and why remains unclear.

Therefore, the aim of this thesis is to develop a single framework that links different models to help in the choice of a sustainable CCU technology for a specific region and quantify its potential environmental benefits. Special focus is given to the methodological considerations in order to minimise the modelling inconsistencies described in this literature review. The Australian economy is used as a case study to demonstrate the application of the framework to uncover the benefits of applying a sustainable CCU alternative to a geographically-relevant process.

### 3 National level analysis, extended input-output analysis



As carbon capture and utilisation (CCU) is a CO<sub>2</sub> mitigation mechanism, the primary criteria of sustainability will be its effect on global warming. Thus, the first step in the systematic method proposed is to analyse a national or regional economy to determine the key areas where a reduction in carbon emissions bears optimal results. The selection of a suitable CCU pathway will be a function of the industry sectors of the economy in which emissions reduction can be accomplished with the least socio-economic impact.

This chapter presents the methodology of an innovative extended input-output analysis model with a multi-objective optimisation, created to examine the complex network of interactions among industry sectors in an economy. The Australian economy was used as a case study to prove the methodological process in identifying these key industry sectors. The model is ultimately capable of mapping an optimal space of scenarios for emission reduction with a minimal socio-economic loss. The results of the case study provide the foundation of the subsequent analyses in Chapter 4 and Chapter 5.

This chapter draws from the content and results published in Rojas Sanchez *et al.* (2019). At the time of publication, this was the first extended IOA model that supports multiple objectives in the optimisation framework.

## 3.1 Background

The intricate relationship between social, economic, and political constraints must be understood to find an optimal pathway to reduce environmental impacts, including anthropogenic greenhouse gas (GHG) emissions. Although new technology developments have the potential to reduce environmental impacts without a considerable socio-economic toll, efficiency-driven technical improvements do not suffice on their own (van Sluisveld et al. 2016). Moreover, those same efficiency improvements have led to increased consumption, offsetting the gained reduction in emissions (Wood 2009). Therefore, the transition to more sustainable practices also necessitates the consideration of lifestyle and consumption pattern changes. Modification to consumption may result in cuts to the production of particular sectors. Such cuts are socially and politically difficult because they may hinder economic growth. For this reason, a complete analysis is necessary to find key areas for emission reduction that incur the least socio-economic impact.

### 3.1.1 Input-output analysis

Input-Output Analysis (IOA) is a powerful tool to analyse the production and consumption patterns of an economy and their corresponding emissions. Introduced by Leontief (1936), input-output (IO) tables map economic flows between different industrial sectors. The basic framework of an IO model is linear equations that show how outputs of different sectors become inputs of others, thus portraying the economic transactions of sectors as producers and consumers. A portion of the total output of a

sector will be sent to other sectors as intermediate demand and the remaining fraction as final demand, which is market sales or consumption. These characteristics render a general model that will react to changes made upon it and will afterwards give insight into the complex wave of consequences across the whole system. IOA proves to be extremely useful since it avoids singling out changes to specific parts of the system while holding everything else constant.

The nature of IOA has led to the incorporation of other data –such as GHG emissions– into the model to analyse them as part of the interdependent system. Leontief (1970) introduced the consideration of the effects of pollution and other undesirable factors in the economic system. As Hertwich and Peters (2009) argued, pollution responsibility is differently distributed depending on the economic configuration of a system. Environmentally-extended input-output (EEIO) models use their interdependent economic framework to trace emissions back to the origin of demand-driven production, thus determining the carbon footprint or indirect emissions of goods and services. This upstream calculation implicitly takes a life cycle approach towards the embodied emissions of industrial activities, using final demand as a functional unit (Wood & Dey 2009). Analyses based on this approach can help find key areas where consumption could be modified or limited.

Several IO works focused on embodied emissions have been developed to meet a particular objective or agenda. Such objectives can be studied through analysis of predefined desired scenarios or through the optimisation of the IO model to approach a set of goals. In the latter case, the usual static approach of IOA is modified to adapt to sensitivity analysis. A precursor of this static relaxation is found in Lixon *et al.* (2008), where output is progressively reduced across all sectors of the Canadian economy according to different policy scenarios until GHG levels met the limits agreed by the Kyoto Protocol (KP).



Later, linear programming (LP) models with Leontief production functions were developed to optimise output levels rather than reduce them uniformly. San Cristóbal (2010) produced a conventional LP model to meet KP reductions on GHGs for Spain by limiting the demand satisfaction of different sectors of the economy. The study maximised total output and constrained emissions to specific percentages of each air pollutant, analysing the demand satisfaction met at that scenario. Later, a bi-objective IO optimisation was elaborated by Pascual-González *et al.* (2016), finding key sectors in the US economy to be regulated to minimise CO<sub>2</sub> emissions at a macroeconomic scale while maximising demand satisfaction. More recently, Nguyen *et al.* (2018) calculated the maximum reduction in GHG emissions through six climate change mitigation scenarios by 2030 in Vietnam. Although it was not an objective within the LP model, the assessment included an evaluation on human health for every scenario. Finally, Lekve Bjelle *et al.* (2018) developed a comprehensive methodology to quantify the extent of possible carbon footprint reduction of Norwegian households towards a 2°C global warming target. Moreover, their LP model optimises the percentage of emissions decrease according to the rebound effect, i.e. re-spending on other goods because of limiting the initial consumption. Rather than focus on alternative technologies, the study aims to understand how household consumption can modify its lifestyle according to different rebound scenarios of varying GHG intensities.

The integration of IOA with optimisation formulations has provided a more reliable analysis for the most adequate configuration of the economic system to meet a particular goal. To the best of my knowledge, there are no current extended IO models in the public domain that support additional objectives in their optimisation framework.

### 3.1.2 Global warming potential

The GHG global warming potential (GWP) metric was created by the Intergovernmental Panel on Climate Change (IPCC) to serve as a useful measure for policy-making and other actions that necessitate a sound comparison among pollutants (IPCC 1990). The GWP of a certain trace gas is a relative measure over a specific time horizon, which compares the warming effect against CO<sub>2</sub> as a reference gas. Therefore, the GWP units are carbon dioxide equivalents (CO<sub>2</sub>e).

The IPCC introduced this concept in their first Scientific Assessment as a tool to help describe the ability of GHG to affect the radiative forcing (*“net radiative flux change induced at the tropopause keeping the concentrations of all other species constant”*) and serve as a useful means to policy-making and other actions that necessitate a sound comparison among pollutants (Shine et al. 1990). GWP depends on the absorption of infrared radiation per unit mass of the gas, the spectral location of its absorbing wavelengths, and its lifetime in the atmosphere. Therefore, a gas can have a high GWP due to the fact of a prolonged lifetime even if it has low radiative forcing. At the same time, this number can change depending on the time horizon chosen (for it is a time-integrated change), on the indirect global warming effects (subsequent production of other GHG throughout a chemical reaction scheme), and even on the composition of the atmosphere itself (Isaksen et al. 2002).

### 3.1.3 Characterisation metrics and time horizon selection

The characterisation metrics used in environmental analyses need to be aligned with a specific timeframe, since they have a significant bearing on the results. As previously mentioned, GWP is a time-integrated relative measure, which is also dependant on the lifetime of the gas and even the composition of the atmosphere itself (Isaksen et al. 2002).

The Kyoto Protocol, Annex A (UNFCCC 1998) lists 6 gases to be GHG, including carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF<sub>6</sub>). The Doha Amendment (UNFCCC 2012) adds nitrogen trifluoride (NF<sub>3</sub>) to the list as well. A compilation on the sources for GHG, its GWP for a 20-year horizon and a 100-year horizon timeframe, and its lifetime in the atmosphere is summarized in Table 3.1.

Table 3.1 Characteristics of greenhouse gasses

Greenhouse gas	Major sources	GWP*		
		20-year	100-year	Lifetime in atmosphere
CO <sub>2</sub> Carbon dioxide	Fossil fuel combustion, solid waste, trees and wood products (deforestation), chemical processes (e.g. cement production)	1	1	**
CH <sub>4</sub> Methane	Fossil fuel combustion, livestock, agriculture, decay of organic waste in landfills	86	34	12.4 years
N <sub>2</sub> O Nitrous oxide	Agriculture (fertiliser application), industrial processes, fossil fuel and biomass combustion, solid waste	268	298	121 years
HFCs Hydrofluorocarbons	Refrigerants, aerosol propellants, foam blowing agents, solvents, fire retardants	< 11,005	<13,856	< 242 years
PFCs Perfluorocarbons	Aluminium production, semiconductor manufacturing	< 8,344	< 12,340	< 50,000 years
SF <sub>6</sub> Sulfur hexafluoride	Electrical transmission equipment, circuit breakers	17,783	26,087	3,200 years
NF <sub>3</sub> Nitrogen trifluoride	Semi-conductor manufacturing	12,987,000	17,885	500 years

\* According to the 20-year and 100-year horizon global warming potentials (GWP) from the Intergovernmental Panel on Climate Change (IPCC), Fifth Assessment Report (AR5) (Myhre et al. 2013) including climate-carbon feedbacks; and the Supplementary Material of Chapter 8 of the same report (Ward et al. 2017)

\*\* No single lifetime can be given, because several natural processes remove carbon dioxide from the atmosphere (mostly dissolved in oceans), making its lifetime behave in a non-exponential manner. See Joos et al. (2013)

Characterisation values are subject to considerable uncertainty due to particular assumptions in the evaluation of GWP, such as the fixed estimation on the variable future lifetime of gases, the dependence on constant concentrations of other species with overlapping spectral bands in the time evaluated, and the calculation of indirect effects towards global warming (Shine et al. 1990). When using CO<sub>2</sub> as a reference, the biggest uncertainty relies on the Impulse Response Function (IRF) which dictates the molecule's path in the atmosphere after its emission (Joos et al. 2013).

Notwithstanding these uncertainties, GWP is able to homogenize GHG and quantify total emissions for the sake of analysis, in contrast to other parameters like Global change in Temperature Potential (GTP) which, according to Myhre *et al.* (2013a), has even greater uncertainties. Therefore, it is essential to choose appropriate GWP values according to a suitable time horizon and from the most recent publications, including all quantifiable components like climate carbon feedback.

## 3.2 Modelling framework

The extended IO model is constructed by integrating economic flows, emissions to the atmosphere, and employment-related data. A variety of indicators are produced to give insight into the role of the sectors in the different areas. This was named the “sectoral analysis”. Later, the multi-objective optimisation (MOO) was formulated. The “bi-objective optimisation” maximised GDP and minimised GHG emissions, and the “tri-objective optimisation” also included employment maximisation. Section 3.2.1 describes the construction of the IO model. Then, sections 3.2.2 and 3.2.3 detail the modelling framework of the sectoral analysis and the MOO, respectively. The description of the case study, data used, and results are shown in Section 3.3 .

### 3.2.1 Input-Output Model

IO models are comprised of interconnected linear equations that represent, commonly in monetary values, the flows within an economy. Equation (3.1) shows the general form of the total output ( $x$ ) of sector  $i$  throughout internal output or demand to  $j$  sectors plus the final demand ( $y$ ) of that sector.

$$x_i = z_{i1} + z_{i2} + \cdots + z_{ij} + y_i \quad (3.1)$$

The components of these equations can be arranged as matrices, e.g. all internal  $z$  flows of the economy as an inter-industry or transaction matrix ( $\mathbf{Z}$ ). An overly simplified visual representation of the matrices in the resulting IO table is shown in Figure 3.1. As rows, sectors can be perceived as consumers having a total output ( $\mathbf{x}$ ) from consumption of other sectors in the transaction matrix ( $\mathbf{Z}$ ) and the final demand matrix ( $\mathbf{y}$ ). The final demand matrix is comprised of vectors for final consumption by households, final consumption by government, gross fixed capital, changes in inventories, and exports. As columns, sectors can be perceived as producers that account for the same total output ( $\mathbf{x}$ ) by the sum of their production to other sectors in  $\mathbf{Z}$ , plus imports ( $\mathbf{m}$ ), and value-added ( $\mathbf{v}_a$ ). The value-added matrix has vectors measuring taxes less subsidies on products, adjustments on exports, value added at basic prices, among other components. This arrangement allows accounting for every economic flow as an input or output of the economy. Finally, to create an extended hybrid IO model, the emissions per sector matrix ( $\mathbf{f}$ ) and the social account matrix ( $\mathbf{s}$ ) are added as rows to correlate them as associated production.

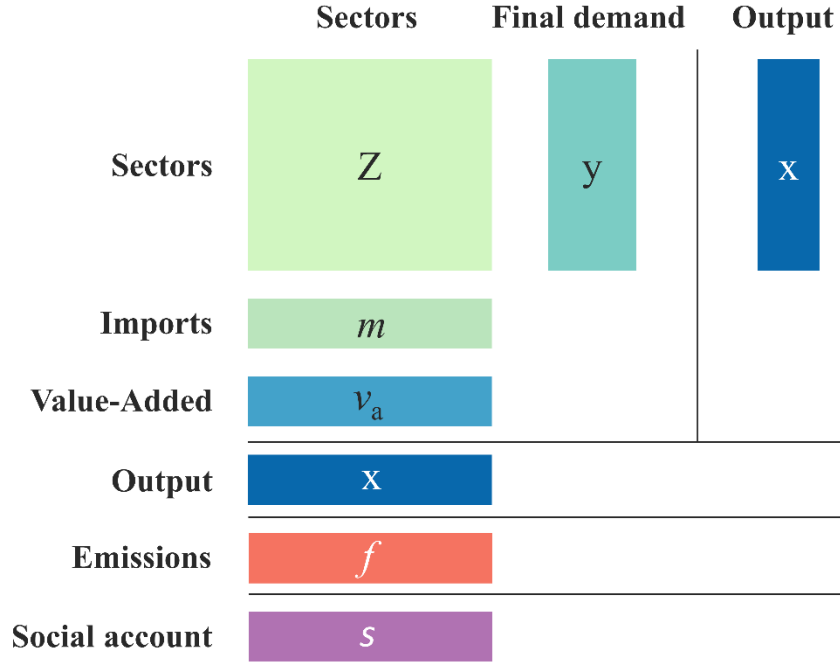


Fig. 3.1 Simplified visual representation of the data arrangement in the extended IO table

Upon having the elements of the transaction matrix ( $Z$ ) and the total output ( $x$ ), the technical coefficients or direct input coefficients ( $a$ ) are obtained, as equation 3.2 shows.

$$a_{ij} = \frac{z_{ij}}{x_j} \Rightarrow z_{ij} = a_{ij}x_j \quad (3.2)$$

Substituting Equation 3.2 in Equation 3.1,

$$x_i = a_{i1}x_1 + a_{i2}x_2 + \dots + a_{ij}x_j + y_i \quad (3.3)$$

And rewritten in matrix format,

$$x = Ax + y \quad (3.4)$$

Then, with simple matrix algebra, equation 3.5 can be obtained, where  $I$  is the identity matrix and the exponent on the parenthesis indicates the inverse of the matrix.

$$y = x(I - A) \Rightarrow x = (I - A)^{-1}y = Ly \quad (3.5)$$

$L$  is the Leontief inverse or total requirements matrix, which is the key to the manipulation and prediction of consequences in the model. The figures in this matrix show all the direct and indirect changes in the model as a consequence of a certain perturbation. By employing the Leontief inverse, any change on output or demand will

produce a specific solution to the system, which is a new scenario consequence of that change in the whole economy.

For the incorporation of air pollution analysis, coefficients of GHG emissions ( $\mathbf{e}$ ) are obtained through the total emissions per sector ( $\mathbf{f}$ ) in emissions inventories per total output of a sector ( $\mathbf{x}$ ). The coefficient vectors for value-added, employment, and other components of the social account matrix were obtained as well by the ratio of their corresponding values per total output of a sector.

$$e_j = \frac{f_j}{x_j} \quad (3.6)$$

This seemingly simple mathematical configuration renders a powerful linear programming engine, where all the relationships between its components can be studied and predictions can be made. It does have, however, certain constraints to it, as Christ (1955) succinctly enumerates. Firstly, the assumption of constant returns to scale. Leontief matrix works with fixed technical coefficients, which means that the ratios of cost of production are constant. Secondly, there is only one process used for the production of a good or service and there cannot be substitution among inputs. This particular assumption excludes optimization in terms of supply. Both assumptions are introduced because of problem simplicity.

### 3.2.2 Sectoral Analysis

There are a number of different indices or multipliers that give insight into the role that each sector plays in the economy. Multipliers are values that quantify the economic impacts derived from a perturbation on the system. These include the direct consequence caused by the initial effects as well as the indirect ripples of the total effects on the economy (Miller & Blair 2009). Depending on the type of perturbation induced, there are many useful multipliers. One of the most common ones is the simple output multiplier –or, as Kowalewski (2009) more comprehensively names it, Sectoral

Production Multiplier (SPM)– which is the total value of production in all sectors to satisfy a dollar worth of final demand of a specific sector. These values are obtained from the following equation for every sector once the IO model is constructed.

$$SPM_j = \sum_{i=1}^n l_{ij} \quad (3.7)$$

The value of  $SPM_j$  indicates the additional total output value of changing the final demand of sector  $j$  by one dollar, including the total indirect effects on the other sectors. Thus, a comparison of SPM in the sectors effectively shows where extra spending or cuts on the demand of output of a sector would have a bigger impact on the whole system.

Other types of multipliers replicate the same mechanism of SPM but, rather than observing changes on output itself, they monitor another aspect that is a function of the output. The employment and value-added multipliers (EM and VAM, respectively) of every sector can be computed by weighting the elements of the Leontief inverse ( $\mathbf{L}$ ) with their corresponding coefficient vector. These will now provide insight into the repercussions of a change in final demand on both areas.

A very useful pair of indices succinctly employed by the Ministry of Internal Affairs and Communications of Japan (2009) are the Index of the Power of Dispersion (IPD) and the Index of the Sensitivity of Dispersion (ISD). The IPD is the ratio of the SPM by the mean of the entire vertical sums, as shown in equation 3.8. This index quantifies the magnitude of sector  $j$ 's final demand in its power to create repercussions on the production of all other sectors. Similarly, the ISD is obtained by attempting the same ratio, but now by summing the rows. This index measures how much a sector is influenced by perturbations in the flows of other sectors.

$$IPD_j = \frac{\sum_i^n l_{ij}}{\frac{1}{n} \sum_i \sum_j l_{ij}} \quad (3.8)$$



$$ISD_j = \frac{\sum_j^n l_{ij}}{\frac{1}{n} \sum_i \sum_j l_{ij}} \quad (3.9)$$

Regarding environmental data, GHG emissions ( $\mathbf{f}$ ) and its coefficients are pertaining only to emissions recorded in the production activities of every sector. To disaggregate these emissions, one can construct the emissions matrix ( $\mathbf{F}$ ) as follows:

$$\mathbf{F} = \hat{\mathbf{e}}\mathbf{L}\hat{\mathbf{y}} \quad (3.10)$$

Equation 3.10 uses the emission coefficients previously obtained and the output in matrix form to produce an environmental matrix that shows the inherent emissions of sectors' activities in every trade within itself or other sectors. In this manner, it can clearly be quantified how much a sector pollutes in the production of its own products ( $\boldsymbol{\varphi}^0$ ), in the production of products for other sectors ( $\boldsymbol{\varphi}^P$ ), and in the production of its own products by using other sectors ( $\boldsymbol{\varphi}^C$ ). The row sums of this matrix (i.e.  $\boldsymbol{\varphi}^0 + \boldsymbol{\varphi}^P$ ) are equal to the emissions recorded on the emissions data ( $\mathbf{f}$ ). These will be considered as the GHG emissions on the producer perspective, since it measures emissions by the activities of a sector regardless of the final destination of its production. On the other hand, the column sums of the matrix (i.e.  $\boldsymbol{\varphi}^0 + \boldsymbol{\varphi}^C$ ) are equal to the GHG emissions on the consumer perspective ( $\mathbf{f}^*$ ), since it measures emissions of its products, whether they were made within the same sector or by using others to do so. Equation 3.10 also gives an environmentally weighted Leontief matrix ( $\hat{\mathbf{e}}\mathbf{L}$ ), which, similar to the SPM, yields multipliers through the sum of its columns. These were named Greenhouse Emission Multipliers (GHEM).

Two ratios were also created to perceive how every sector distributes its emissions according to both producer and consumer approaches. The Greenhouse Output Ratio (GHOR) measures how much of the total output emissions come from the demand of other sectors by using that sector. Greenhouse Input Ratio (GHIR)

measures instead how much of the consumer emissions come from employing other sectors rather than itself.

$$GHOR_j = \frac{\varphi_j^P}{f_j} \quad (3.11)$$

$$GHIR_j = \frac{\varphi_j^C}{f_j^*} \quad (3.12)$$

### 3.2.3 Multi-objective optimisation

The IO model, albeit complex in the amount of flows, is ultimately linear. Therefore, the integration of an IO model with a socio-economic and environmental framework will lead to a multi-objective linear programming (MOLP) problem. An efficient methodology to solve MOLP is Benson's algorithm (Benson 1998a). This method produces an n-dimensional set of all optimal extreme points or vertices of the feasible outcome polyhedron of a problem. It also provides the weakly efficient points in the outcome set, further increasing the available optimal spectrum for the decision maker. The detailed description of the algorithm is provided elsewhere (Benson 1998b). BENSOLVE is a powerful GNU General Public License software package developed by Löhne and Weißing (2017) that solves Vector Linear Programs (VLP) –a more general form of MOLP– based on Benson's algorithm and its extensions. Equivalent to polyhedral projection, the VLP solver produces the vertices and extreme directions of the optimal solution set by obtaining all the solution images defined by a polyhedral cone of the objective vectors within an n-dimensional polyhedron of the feasible set of points,  $\mathbf{S}$ . This particular MOLP model is then defined as,

$$\min \mathbf{P}\mathbf{x} \quad s.t. \quad \mathbf{x} \in \mathbf{S} \quad (3.13)$$

where  $\mathbf{S}$  is the feasible set in the form of a polyhedron defined, in general terms, by,

$$\mathbf{S} = \{\mathbf{M}\mathbf{x}: \mathbf{l} \leq \mathbf{x} \leq \mathbf{u}, \mathbf{a} \leq \mathbf{B}\mathbf{x} \leq \mathbf{b}\} \quad (3.14)$$

For this specific model, the inequality  $a \leq Bx \leq b$  would be equivalent to the following equation:

$$\alpha y_0 \leq [I - A]x \leq y_0 \quad (3.15)$$

Equation 3.15 serves as an upper and lower bound on final demand. At the upper constraint, the values of demand are topped at the original levels of final consumption ( $y_0$ ). At the lower constraint, they are capped by a percentage ( $\alpha$ ) of the original demand. This was implemented to avoid non-positive outputs or demands, and to ensure that a certain percentage of demand for every sector is at least satisfied. It should be evident that this same equation makes the initial lower and upper bounds on  $x$  of equation 3.14 redundant. Finally,  $P$  is the objective matrix, shown in equation 3.16, where  $v_a$ ,  $e$ , and  $\sigma$ , are the coefficient vectors of value-added, GHG emissions, and employment, respectively.

$$P = \begin{bmatrix} -v_a \\ e \\ -\sigma \end{bmatrix} \quad (3.16)$$

GDP is maximised through the sum of the value-added components of each sector by using the static vector of value-added coefficients ( $v_a$ ) and the variable output vector ( $x$ ). According to the NACE Rev. 2 (European Commission 2008), gross value added at basic prices is total output minus intermediate consumption (including in it taxes on products and imports without subsidies on products), which is the additive component of each economic sector to GDP. Since the MOLP algorithm solves the minimisation problem, the maximisation of the objectives is obtained by using the negative coefficient vectors of value-added and employment. The bi-objective optimisation will only include value-added and emissions in the objective matrix, while the tri-objective optimisation will include all three parameters.

This method does not intend to disaggregate types of goods and services within a sector. Final consumption will be quantified as the entire gross final demand for every sector in the economy, regardless of the destination of that particular demand or the

characteristic of the product (e.g. luxury vs. basic goods). Consequently, there are no interdependencies between prices and quantities. As a result, this model does not account for the rebound effect associated with consumption limitation. The rebound effect, as an increase in energy consumption linked to technological improvements and lower associated prices (Brookes 1990), may have an effect in the corresponding environmental impact of other activities (Hertwich 2005). Its direct effects in household level (Lekve Bjelle et al. 2018) or in indirect macroeconomic effects (Thomas & Azevedo 2013) can play a role in the offset of GHG emissions initially avoided (Druckman & Jackson 2009). But as Garnaut (2008) also mentioned, quantifying accurately the effects on consumption patterns draws on human behaviour and judgement. Thus, notwithstanding its importance, the rebound effect and other behavioural measures are not estimated in this model. It is the objective of this methodology and sensitivity analysis to maintain the approach as broad, objective, and mechanical as possible.

### 3.3 Case study of the Australian economy

#### 3.3.1 Background and literature review

The case study for this model is the Australian economy. A number of IO studies have been carried out for Australia over almost 40 years ago. James (1980) performed one of the first IO studies for Australia, proposing an energy framework to be used for forecast scenarios. Years later, Common and Salma (1992) focused on calculating CO<sub>2</sub> emissions from fossil fuel combustion. Lenzen (1998) then provided a complete and pioneering analysis on energy and GHG embodiments on goods and services that fulfilled the Australian final demand of 1992/1993. This work differed from Common and Salma's in that it included CH<sub>4</sub> and N<sub>2</sub>O, it introduced a consumption-based perspective in the results scheme, and it also used physical units rather than all monetary values to avoid distortion by different energy prices for users. Lenzen's (1998)

IO tables were constructed according to different sources in an effort to disaggregate contributions of energy and emissions to every part of final and intermediate consumption. The study also highlighted the limited disaggregation of sectors and the unavailability of GWP values for other gases.

More recently, Wood and Lenzen (2009) performed a thorough analysis on the general concepts used in IOA, indicating that the Australian economy has become more diverse, but the specialisation of the resource flows has increased. Hence, the environmental impacts of most industries are outsourced to a small number of sectors, thus emphasising the need for a life-cycle approach to assess pollution responsibility. Later, Wood and Dey (2009) developed a detailed assessment on Australia's carbon footprint through an IO model with an extensive sectoral resolution, highlighting the importance of transitioning to "greener" consumption through key sectors in the economy. The study also stressed the definition of a good policy by boosting production of sectors with minimum environmental impacts and significant socio-economic weight. Therefore, in this case study, the model computes a multi-objective optimisation on all sectors of the Australian economy using IOA to categorise the sectors according to the previous criteria and locate key areas of focus for consumption limitation.

### 3.3.2 Data considerations

All the data used for this analysis were obtained from different accounts of the World Input-Output Database (WIOD) (Timmer et al. 2015). The air emissions data do not include Land Use, Land Use Change and Forestry (LULUCF) related emissions. As Lifset (2009) mentions, environmental data are very rarely in sync with the scope of other IO tables, evidenced in the delayed release of emissions accounts. Therefore, the data used in this analysis was chosen from the latest available year in all datasets: 2009. The exchange rate used by WIOD for that year is \$0.7913 USD per AUD. The sectors were aggregated in an effort to preserve the highest level of discernible detail.

The result was a 34-sector aggregation for the economy coupled with a classification and abbreviation that indicates the content of every sector. Appendix A includes a correspondence between the aggregated nomenclature, the International Standard Industrial Classification of all economic activities (ISIC), and the Australian and New Zealand Standard Industrial Classification (ANZSIC) (ABS 2006) (cat. no. 1292.0).

The GWP values used in this study are for a 20-year horizon including climate carbon feedback obtained from the AR5 of the IPCC: 86 and 268 CO<sub>2</sub>e for CH<sub>4</sub> and N<sub>2</sub>O, respectively. Commonly, CO<sub>2</sub>e emissions officially published, as those of the National Greenhouse Gas Inventory (Australian Department of the Environment 2012) tacitly use values for a 100-year horizon without climate-carbon feedback from previous assessments reports of the IPCC. The Australian Government specifically uses values from the 2<sup>nd</sup> Assessment Report of the IPCC (1996): 21 and 310 for CH<sub>4</sub> and N<sub>2</sub>O, respectively. This results in a considerably lower total amount of CO<sub>2</sub>-e emissions, also giving more weight to N<sub>2</sub>O but much less to CH<sub>4</sub> emissions. This paper instead uses 20-year horizon GWP values for two reasons. Firstly, actions towards sustainability need to be established on a shorter span than 100 years. Therefore, analysis of the economic activities –or lack thereof– and their polluting emissions need to be correspondingly quantified on a shorter period scheme. Secondly, as Reisinger *et al.* (2010) argued, uncertainties on GWP values increase with the time horizon. Thus, selecting a shorter time horizon reduces uncertainties. Climate-carbon feedback is also included to further represent the full extent of the consequences of emissions. If other GWP values would have been used, results would differ considerably not only in the amount of emissions but also in the influence of each sector in the whole system.

### 3.3.3 Results of sectoral analysis

Figure 3.2 shows the values of the multipliers considered for all sectors. The units for SPM, VAM, and EM are the total monetary value of output, of value-added, and tens

of employees, respectively, per one USD worth of change in the final demand. As mentioned, the comparison between values within a type of multiplier gives insight into the magnitude of the total perturbation on the economy of each sector. At the same time, this table shows the ranking of each sector in descending order through the different multipliers. Lines are added to aid in the appreciation of movement in ranking on the lists. These changes in position serve to portray the difference of influence of a sector according to every parameter. Moreover, it proves how the sectors with the highest effect on output do not have an equally high influence on GDP, or how these also do not necessarily hold the same pattern on their influence on employment.

Sectoral Production			Value-added		Employment	
1. Food&Tobacco	2.35		1. Prof. Services	2.97	1. Prof. Services	3.68
2. Construction	2.32		2. Finance&Ins.	1.82	2. Households	2.09
3. Wood Products	2.15		3. Mining	1.26	3. Oth. Mfg.	2.04
4. Metals	2.15		4. Real Estate	1.23	4. Motor Whole.	1.65
5. Trnsp. Mfg.	2.09		5. Oth. Whole.	1.19	5. Retail Trade	1.63
6. Non-metals	2.07		6. Construction	1.06	6. Oth. Whole.	1.48
7. Chem.&Pharm.	2.07		7. Supp. Trnsp.	0.95	7. Finance&Ins.	1.46
8. Petro.&Nuclear	2.06		8. Agriculture	0.94	8. Healthcare	1.45
9. Oth. Mfg.	2.05		9. Utilities Supply	0.94	9. Hotel Services	1.43
10. Air Trnsp.	2.05		10. Telecomms.	0.94	10. Education	1.39
11. Hotel Services	2.02		11. Metals	0.87	11. Waste Mgt.	1.29
12. Water Trnsp.	2.00		12. Land Trnsp.	0.84	12. Metals	1.18
13. Utilities Supply	1.98		13. Retail Trade	0.82	13. Construction	1.11
14. Agriculture	1.95		14. Healthcare	0.81	14. Agriculture	1.05
15. Motor Whole.	1.94		15. Education	0.81	15. Land Trnsp.	1.04
16. Waste Mgt.	1.93		16. Pulp&Paper	0.78	16. Telecomms.	1.04
17. Plastics	1.91		17. Defence	0.76	17. Defence	0.96
18. Telecomms.	1.91		18. Households	0.72	18. Food&Tobacco	0.92
19. Oth. Mach.	1.90		19. Waste Mgt.	0.71	19. Supp. Trnsp.	0.81
20. Oth. Whole.	1.90		20. Food&Tobacco	0.63	20. Mining	0.81
21. Supp. Trnsp.	1.90		21. Chem.&Pharm.	0.60	21. Pulp&Paper	0.80
22. Prof. Services	1.88		22. Hotel Services	0.59	22. Utilities Supply	0.79
23. Land Trnsp.	1.87		23. Air Trnsp.	0.57	23. Wood Products	0.78
24. Pulp&Paper	1.85		24. Water Trnsp.	0.55	24. Real Estate	0.76
25. Textile	1.82		25. Plastics	0.53	25. Trnsp. Mfg.	0.73
26. Elec.&Opt. Eq.	1.81		26. Trnsp. Mfg.	0.53	26. Textile	0.66
27. Retail Trade	1.75		27. Motor Whole.	0.53	27. Air Trnsp.	0.57
28. Defence	1.73		28. Elec.&Opt. Eq.	0.51	28. Elec.&Opt. Eq.	0.57
29. Mining	1.67		29. Non-metals	0.51	29. Oth. Mach.	0.56
30. Finance&Ins.	1.57		30. Wood Products	0.49	30. Chem.&Pharm.	0.53
31. Real Estate	1.54		31. Petro.&Nuclear	0.48	31. Plastics	0.49
32. Households	1.50		32. Oth. Mach.	0.46	32. Non-metals	0.46
33. Education	1.42		33. Textile	0.45	33. Water Trnsp.	0.33
34. Healthcare	1.34		34. Oth. Mfg.	0.41	34. Petro.&Nuclear	0.31

Fig. 3.2 Ranked lists of Sectoral Production, Value-added, and Employment multipliers

The correlation of the abbreviations (used here and henceforth in the following figures) with the full name of the sectors can be found in Appendix A. Units for SPM, VAM, and EM are USD worth of output, of value-added, and tens of employees, respectively, by one USD change of final demand. Lines help visualise the changes in ranking among multipliers

In terms of the SPM, the highest values are those of the “Food, Beverage and Tobacco”, “Construction”, and “Wood Products” sectors. This would indicate that an investment in the final consumption of one of these sectors (e.g. government spending) would result in the biggest economic growth in terms of output of all other sectors considered. Nevertheless, as also highlighted by West (1999), multipliers are relative so they can sometimes mislead on a cause-effect relationship and misinterpret the true magnitude of the effect (i.e. small multipliers can correspond to a large economic impact and vice versa). At the same time, effects can be overstated when the sector studied is at near full capacity and will not have the same outcome as foreseen, falling into shifts of imports/exports (Miller & Blair 2009). Despite this cautionary warning, SPM still gives an estimate of the economic magnitude of every sector towards the whole economy.

In terms of the other multipliers, “Professional, Scientific, Technical and Information Services” ranks first, since it contains the vast majority of professions in society and has a direct relationship to services that create value in the economy. It is worth noting how sectors like “Finance and Insurance Services” or “Other Wholesaling” rank among the first positions in terms of value-added, but would not have a high increment in employment. The complete opposite behaviour is seen for sectors like “Motor Vehicle Wholesaling” and “Other Manufacturing; Recycling” with high impact on employment, but less on value-added. Sectors like “Mining” and “Real Estate Services” have a big impact on value-added but not on the total number of jobs created.

The use of the indices is crucial to fully compare the sectors’ influence upon each other and globally. Figure 3.3 is a chart that places sectors into quadrants according to their IPD and ISD values. As it was previously detailed, these indices show the relative influence on other sectors or on themselves by other sectors.

The sectors in quadrant ‘**I**’ have high influence on other industries and are also sensitive to changes in the economy surrounding them. These should typically be the



raw materials manufacturing sectors, like “Basic and Fabricated Metals” and “Construction”, which depend much on the economic flows of other sectors but can themselves also create a wave of consequence upon others. It can be seen as well that sectors like “Agriculture, Forestry, and Fishing” and “Electricity, Gas, and Water Supply” (abbreviated “Utilities Supply”) are also present in this quadrant, which shows that they have a greater influence over the economy. Sectors in quadrant ‘**II**’ have little influence on others but are highly affected by activities of other sectors. These are traditionally sectors that provide services, like “Finance and Insurance Services” and “Professional, Scientific, Technical and Information Services” (sector with the highest ISD). All of these depend greatly on the sectors to which they provide their service. “Mining”, however, is also present in this quadrant, indicating that it is very sensitive to changes in the economy. This should not be unexpected with Australia’s heavy mining activities and manufacturing that comes through it.

Sectors in quadrant ‘**III**’ do not have a high influence on others and are also not greatly influenced by others. These are virtually independent sectors, as “Health Care and Social Assistance” (sector with the lowest IPD), “Education”, and “Private Households with Employed Persons” (sector with the lowest ISD), all of which continue to undergo operations regardless of small changes in other sectors. Finally, sectors in quadrant ‘**IV**’ have a strong effect over others but are mildly influenced by changes. These should be sectors that focus on goods to end consumers, such as “Wood Products”, “Food, Beverages, and Tobacco” (sector with the highest IPD), and “Other Manufacturing; Recycling”. These multipliers and indices should serve as a glimpse on the configuration of the Australian economy and its interconnections, indicating the relative magnitude of change to different areas according to a perturbation in final demand or consumption of each sector.

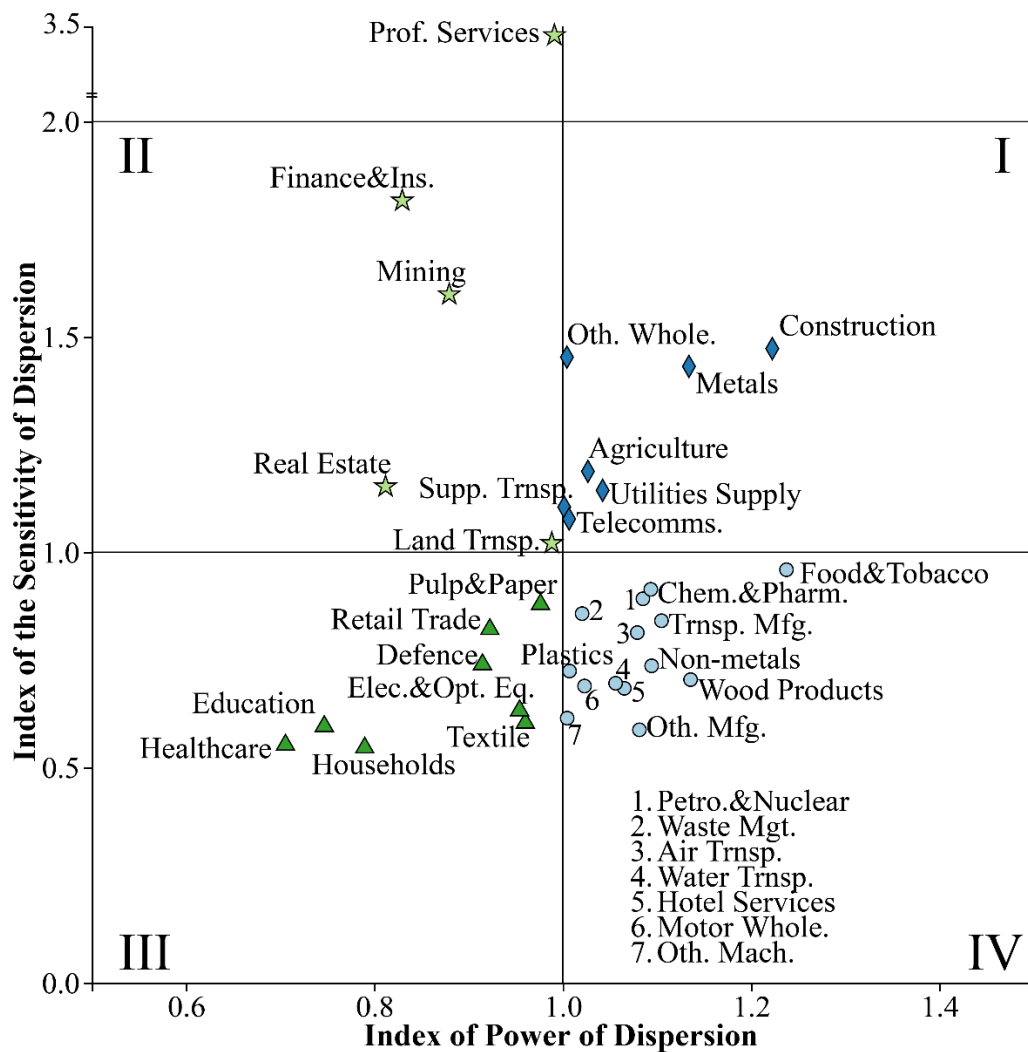


Fig. 3.3 Distribution of sectors in four quadrants based on their index of the power of dispersion (IPD) and the index of the sensitivity of dispersion (ISD)

To assist in the emissions analysis, the GHEM was created and compared with the emissions coefficients,  $e$ . The importance of this multiplier resides in the different origin of economic perturbation that brings a change in emissions. The emissions coefficient ( $e$ ) gives a magnitude of the emissions change according to one USD worth of change in the total output of a sector, whereas GHEM provides it according to one USD worth of change in the final demand of a sector, which obeys the intrinsic economic configuration of the economy.

Figure 3.4 shows the ranked list of sectors for both values, with lines to aid in perceiving the changes in position between both lists. “Agriculture, Forestry, and

Fishing” and “Electricity, Gas, and Water Supply” are highest in both rankings by a considerable difference, proving to be emission intensive in their activities. But sectors like “Food, Beverages, and Tobacco” and “Wood Products” that do not seemingly have a high emission intensity on their own activities, do have a high GHEM ranking, indicating that they use other sectors that have high-level emission intensity to satisfy their demand.

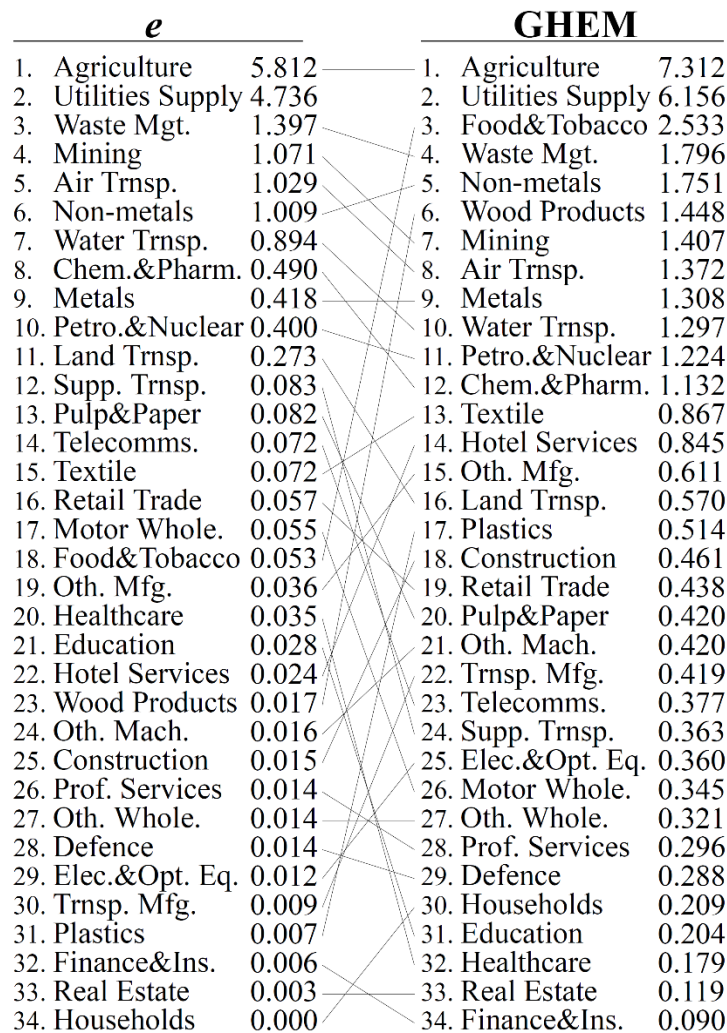


Fig. 3.4 Ranked lists of greenhouse emission coefficients (*e*) and greenhouse emission multipliers (GHEM). Units are tonnes of CO<sub>2</sub>-e per one thousand USD worth of output and final demand, respectively.

Multipliers, however, are relative and do not show the full magnitude of the environmental strain. Figure 3.5 shows the total emissions of every sector in descending order according to a producer (left chart) and consumer (right chart) perspective. The

lines connecting the sectors are provided to help visualise the change of ranking between the two perspectives. Although “Agriculture, Forestry, and Fishing” is the most contributing sector in both perspectives, its associated GHG emissions decrease considerably on the consumer perspective. “Mining” instead rises to 2<sup>nd</sup> place by overtaking “Electricity, Gas, and Water Supply”. Moreover, seemingly inoffensive sectors like “Accommodation and Food Services” (abbreviated “Hotel Services”) increase considerably in ranking while producer emission- intensive sectors like “Non-Metallic Minerals” are one of the lowest in the consumer categorisation. It seems that, while there is a very pronounced curve on the left bar chart, the emissions are more homogenised when distributed by consumers. As producers, the activities of only 4 sectors produce more than 80% of total emissions; whereas, as consumers, that same percentage of emissions is only met until the 9<sup>th</sup> sector.<sup>1</sup> A consumer-based analysis differs greatly from a producer based one, giving much more insight on the true responsibility of pollution.

---

<sup>1</sup> Percentages by also considering emissions of Final consumption expenditure by households, which is not plotted in the bar charts and has a calculated value of 46.3 Mt CO<sub>2</sub>-e

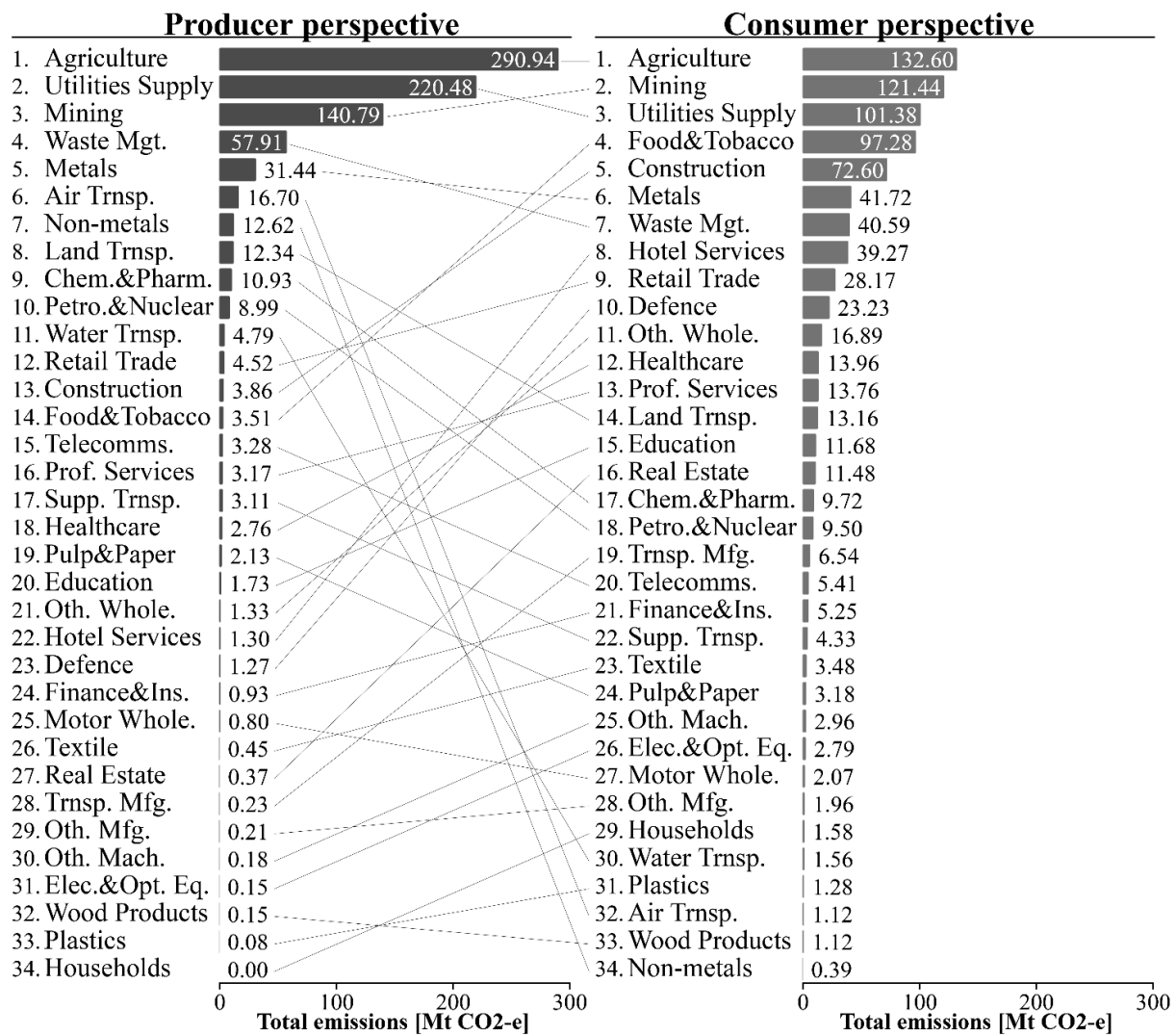


Fig. 3.5 Greenhouse gas emissions on a producer (left) vs a consumer (right) perspective

Finally, Figure 3.6 distributes the sectors according to their GHIR and GHOR values, with aiding dashed lines through the 0.5 ratio on each axis, dividing sectors again into quadrants. Being on a position right or top of the dashed line indicates that the emissions of activities for or by other sectors, respectively, are greater than the emissions of the activities of that sector for its own products.

Sectors in quadrant ‘I’ have a high value of both ratios, indicating that their production emissions for their own products is low and most of both their consumer-based and producer-based emissions come from other sectors. These are sectors like “Wood Products”, “Rubbers and Plastic”, and “Professional, Scientific, Technical and

Information Services”, which necessitate other sectors for their end-user products, but are still themselves a medium that other sectors use to finish their own products. Sectors in quadrant **‘II’** have a high GHOR value, indicating that they emit more by doing activities for other sectors than their own, but have a low GHIR value, showing that their own activities’ emissions are mostly responsible for the production of their own goods. In this quadrant, sectors like “Air Transport”, “Non-metallic Minerals”, and “Water Transport” undergo activities of other sectors’ demand and have comparatively lower emissions from activities of their own consumption. Nevertheless, these ratios are relative, and the true magnitude of emissions can be considerable even when ratio values are small. In this same quadrant but closer to the half GHOR line, “Agriculture, Forestry, and Fishing” and “Electricity, Gas, and Water Supply” are responsible for almost all emissions of their products but also pollute almost as much as their own activities in production for other sectors. This should imply that a reduction of activities in these two sectors would present a bonus in GHG reduction by also cutting emissions from the sectors that depend on them.

Sectors in quadrant **‘III’** emit more than half of their total emissions, either by a producer or consumer approach, from activities for their own consumption. “Mining” and “Waste Collection, Treatment and Disposal Services; Other Social and Personal Services” are found here, since most of their activities are emission intensive and are pertinent to their own consumption scheme. Finally, sectors in quadrant **‘IV’** have a high GHIR value, indicating that they emit more by using other sectors for their demand than what they do on their own activities, but have a low GHOR value, stipulating that most of their production activities’ emissions are for their own goods. These are typically sectors like “Health Care and Social Assistance”, “Education”, “Public Administration and Safety”, and “Accommodation and Food Services”, which use a wide array of sectors to accomplish their activities, but have most of their emissions accountable for their own demand and very little towards that of other

sectors (with the extreme case of Private Households with Employed Persons that does not have recorded output emissions but does have accountable emissions as a consumer).

While the majority of sectors are placed in quadrants 'I' and 'IV', the most polluting sectors from a production perspective are in quadrants 'II' and 'III'. Considering the actual emission numbers, Australia proves to be a heavy GHG polluting country in terms of primary activities sectors. Nevertheless, the emissions responsibility scale is considerably rebalanced when a consumer approach is taken, consequence of a high presence of sectors that have a high ratio of usage of other sectors for their own products or services.

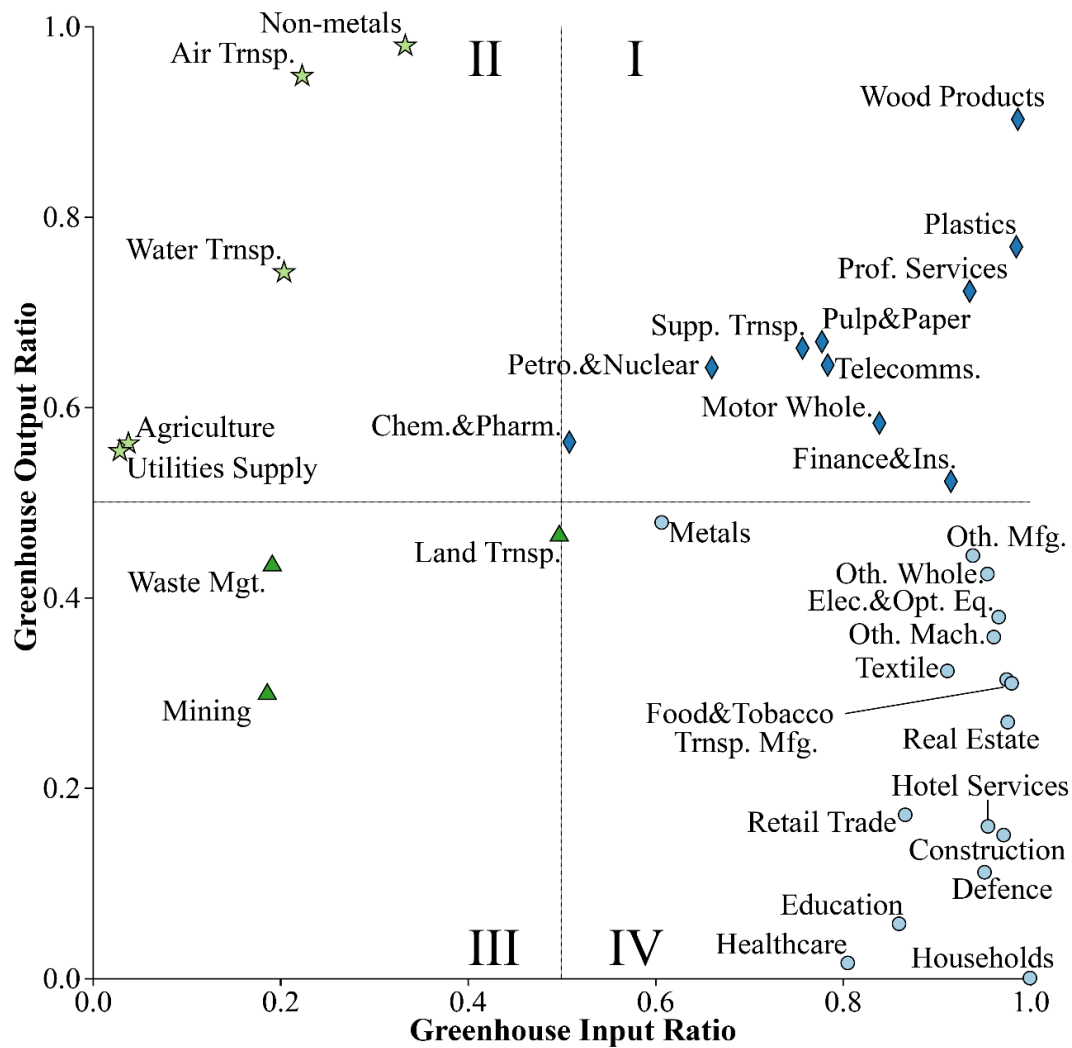


Fig. 3.6 Distribution of sectors in quadrants based on their greenhouse input ratio (GHIR) and greenhouse output ratio (GHOR)

### 3.3.4 Bi-objective optimisation

The previous indicators are useful to identify key sectors according to their influence on a particular parameter studied. But they are relative and, thus, do not necessarily provide the full extent of the ripple of consequences. Furthermore, they are not iterative, making their values inaccurate when multiple progressive changes are done to the economic system. Being inefficient to continuously recalculate multipliers and analyse them individually, an optimisation model instead can inherently consider all parameters and produce the most suitable configuration of the system at every variable scenario.



The optimisation model was solved through Bendsolve Tools, an Octave/MATLAB toolbox from BENSOLVE. As it was mentioned in the modelling framework, a satisfaction ratio ( $\alpha$ ) was employed as a lower bound to ensure that a certain percentage of every sector's demand is met. The results herein use  $\alpha = 0.9$ , proportion also employed by Pascual-González *et al.* (2016), to permit only a 10% variation on consumption levels. The resulting Pareto curve is shown in Figure 3.7, with GDP in its horizontal axis, showing its characteristic form of bi-objective minimisation. The black line is the non-dominated Pareto front, while the grey area indicates all weakly-dominated points. It is evident how a decrease in total emissions incurs a decrease in GDP. In 2009, GDP was valued in 977 bUSD, and emissions were calculated in 890 Mt CO<sub>2</sub>-e.

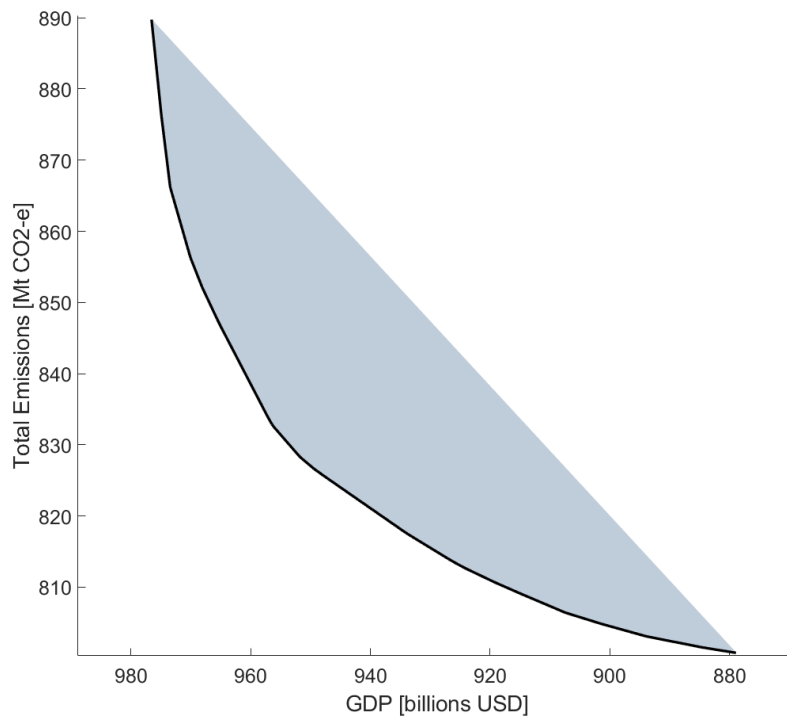


Fig. 3.7 Pareto front, GDP vs Total emissions

The model was re-formatted as an epsilon-constraint bi-objective optimisation to perform a sensitivity analysis. This method defines one of the objectives as a constraint with a fixed target, which emulates a minimization on the solution approximation. The following LP model was created as follows:

$$\max \quad v_a x \quad (3.17)$$

$$s. t. \quad ex \leq \varepsilon \quad (3.18)$$

$$\alpha y_0 \leq [I - A]x \leq y_0 \quad (3.19)$$

The second objective function is transformed into the inequality 3.18, which states that the total emissions produced from the vector of GHG emissions coefficient ( $e$ ), and the output vector ( $x$ ) are limited to a certain emissions target ( $\varepsilon$ ). By modifying  $\varepsilon$  progressively, the sensitivity analysis detected specific changes in slope, indicating when a new sector starts to reduce its final demand. The results revealed that in an optimised scenario of reduction in total emissions, a sector's demand is cut until it reaches its capped level, and the model then jumps to the next sector to continue decreasing demand. When these same results are restructured to show on the horizontal axis the reduction to total emissions rather than the total emissions themselves, this pattern can be better observed. Figure 3.8 shows the decrease of GDP (thicker and darker curve) as a function of the reduction in total emissions, indicating the order of sectors of whose final demand is cut.

Reductions are first achieved through cuts on demand to the “Agriculture, Forestry, and Fishing” sector, until its limit indicated by the point and number ‘1’, which represents a total reduction of 10% of this sector's final demand. If more reduction in emissions is needed, cuts will now be implemented to the “Electricity, Gas, and Water Supply” sector as well, until it reaches its limit at point ‘2’, and so on. The optimisation shows that a determinate amount of reduction to total emissions will entitle a cut on demand to the sector corresponding to the segment of the curve in which the point is located, and all other sectors before it. For instance, a decrease of 50 Mt CO<sub>2</sub>-e would be located in the curve between numbers 9 and 10, indicating a partial cut (5.5%) on demand of the “Mining” sector, and a full 10% cut on demands of sectors 1-9, with a total GDP loss of 15.8 billion USD (decrease of 1.6%). It should be apparent to the reader that a modification on the value of demand satisfaction ( $\alpha$ ),

would modify the cap on the lower bound of demand, allowing more or less reduction to the sector's demand and reducing total emissions and GDP by the same magnitude, without modifying the order of sectors.

Since GDP decreases at different rates through the segments, the rate of economic loss related to a reduction in emissions increases progressively as more sectors are limited. To further explore this pattern, Figure 3.8 includes the unitary GDP loss in USD per kg of CO<sub>2</sub>-e reduced (thinner lighter curve) as a function of total reduction on emissions. This plot helps to visualise how the inherent economic loss of preventing the emission of one kilogram of CO<sub>2</sub>-e grows exponentially. When only cutting demand on the “Agriculture, Forestry, and Fishing” sector, the unitary GDP loss is constant on \$0.12 USD/kg CO<sub>2</sub>-e, result of a perfectly linear decrease on output and, thus, GDP. But when more sectors are included, the unitary GDP loss is no longer constant for every segment, since the interconnections of the economy create a wave of consequences from the initial perturbation.

The results show the optimised order of sectors to be limited in consumption, identifying within the intricate configuration of the economy the full weight that each sector has in terms of GDP when trying to meet an environmental target. Although the optimal order of the model shares similarities with the rankings obtained through the previous indicators, none of them gives the same exact configuration. “Agriculture, Forestry, and Fishing” and “Electricity, Gas, and Water Supply” featured on the top of every list, as a consequence of their high relative and absolute emissions, their high power and sensitivity for dispersion, and their identified proximity to the half GHOR line. Other sectors, however, may not be as straightforward to order correctly according to their accumulated analysis of multipliers and indices. Although the GHEM ranking most resembles the optimal list, only the optimisation model is able to correctly account for all parameters and produce the most suitable order of sectors.

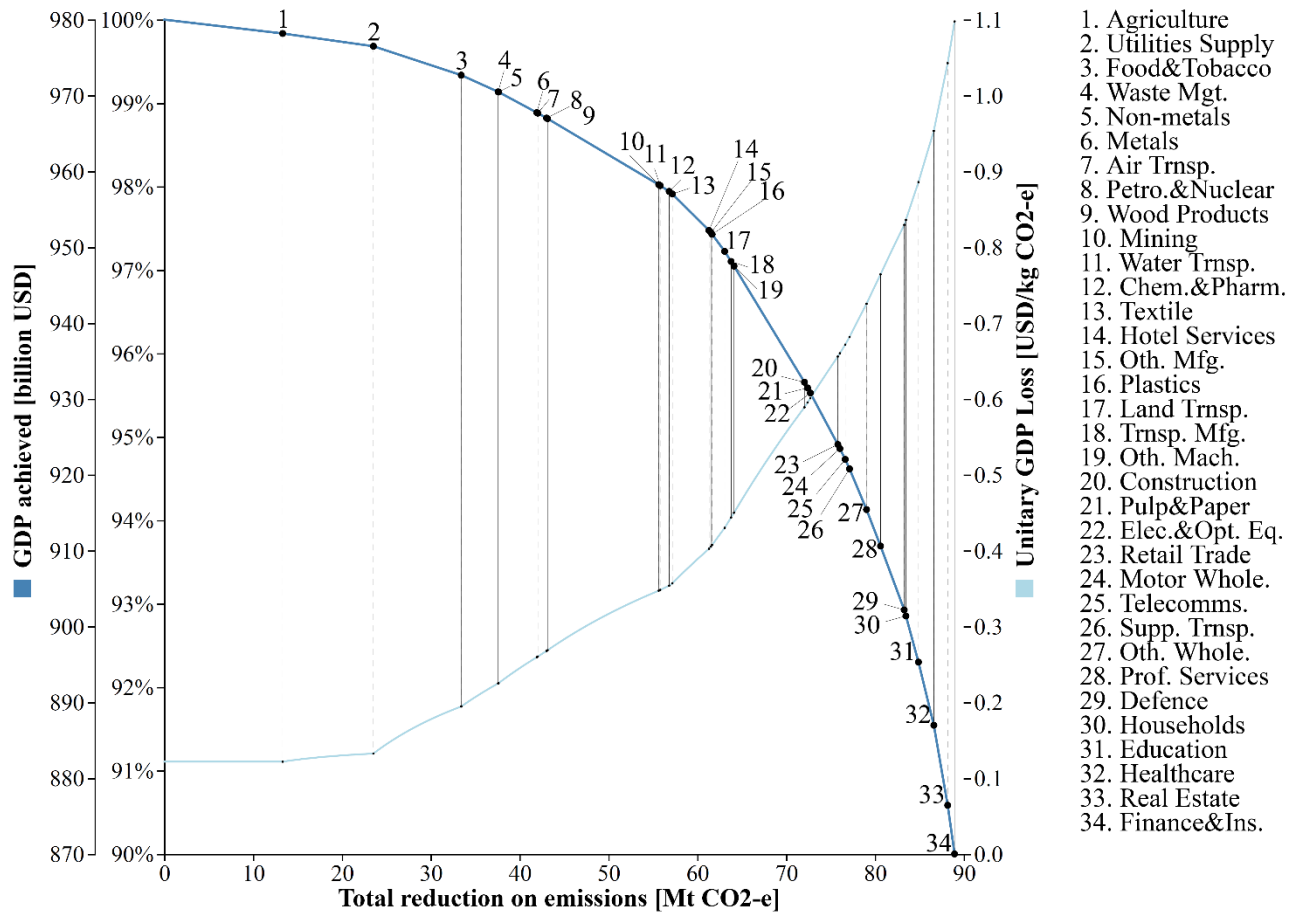


Fig. 3.8 Interaction between emission reduction, GDP achieved [in billion USD and percentage of original GDP level] (left axes, thick dark blue curve) and unitary GDP loss [USD per kg CO<sub>2</sub>-e reduced] (right axis, thin light blue curve)

### 3.3.5 Tri-objective optimisation

By including the employment coefficient vector into the objective matrix of the MOLP, the solution will now map a path that further modifies the sectors' final demand to maximise employment levels in the economy. The primal optimal solution is a three-dimensional polyhedron of 117 vertices, shown in Figure 3.9. Vertices and lines are optimal points, and the grey surfaces are areas of weakly efficient points. The 2D projections for every pair of axes are included in the figure to further help in visualising the complete shape of the polyhedron.

Evidently, employment is directly proportional to GDP and total emissions: more employment causes more activity, which produces more emissions and increases

GDP. However, this mapped Pareto front is not as straightforward as in the bi-objective optimisation. The inclusion of an additional parameter opens the solution set to multiple scenarios where a particular criterion is given more weight. At the start of reducing emissions, there is a similar clear correlation to sectors with the biggest impact, leaving not much choice of possible optimal scenarios. In this optimisation, the first sector to be limited is “Electricity, Gas, and Water Supply”, up to a reduction of approximately 10 Mt CO<sub>2</sub>-e. Reducing the demand of this sector first instead of “Agriculture, Forestry, and Fishing” (like in the previous optimisation) incurs a lower employment and GDP loss but also at a milder reduction on emissions, reason why it is favoured now that there are three objectives to satisfy. Nevertheless, if the required reduction to total emissions is increased, the demand satisfaction of “Electricity, Gas, and Water Supply” is again progressively increased while the “Agriculture, Forestry, and Fishing” sector starts to cut on its demand. Consequently, at reducing approximately 13 Mt CO<sub>2</sub>-e, the first sector has again a 100% demand satisfaction while the second sector is capped until its limit. This same pattern continues in a permutational nature through the array of vertices, providing multiple optimal scenarios.

By further decreasing emissions, the polyhedron branches into multiple regions that expand the available options according to the desired parameters. The sectors are, therefore, not assigned to a particular linear order as in the previous optimisation. A sector whose demand was limited at a particular emissions reduction will not necessarily be limited at a scenario of higher reduction. For example, at a desired reduction of 24.5 Mt CO<sub>2</sub>-e, “Electricity, Gas, and Water Supply”, “Agriculture, Forestry, and Fishing”, and “Coke, Petroleum Products and Nuclear Fuel” are capped exactly to 90% satisfaction of their final demand, incurring an economic loss of 3.7 billion USD (0.4% of total GDP) and a decrease of 25,000 employees (0.3% of total employment). If a higher reduction were needed, the optimal course of action would be

to remove partially the cap on “Coke, Petroleum Products and Nuclear Fuel” and begin limiting the activities of “Food, Beverages, and Tobacco”. The selection of the cap percentage on each sector, however, depends on the particular decision criteria wanted. Limiting the “Coke, Petroleum Products and Nuclear Fuel” reduces emissions at a higher rate and incurs a lower employment reduction rate, but at a more substantial GDP loss.

The best scenario will be chosen according to which parameter is given more weight, in addition to other selection criteria not contemplated in the mathematical model, such as technical, governmental, or trade constraints. It is important to mention that, although the Pareto front may look continuous, it is actually a series of discrete points. A selected reduction on emissions will provide a number of different scenarios to be chosen at a particular point. The model proves to be extremely useful in mapping the array of all optimal possible solutions and providing the specific configuration of demand cuts in sectors once a specific range of the three objectives is decided. This configuration suggests sectors for possible modification or cut to consumption to accomplish a reduction on emissions with the least possible impact on employment and GDP.

If other GWP values for the gases had been used, the results would form a considerably different solution. Using the GWP values employed by the Australian Government (28 and 310 for  $\text{CH}_4$  and  $\text{N}_2\text{O}$ , respectively (IPCC 1996)) within the model would have given more weight to sectors that emit nitrous oxide but would have substantially underestimated the impact of sectors that have high methane emissions. In that scenario, the solution would be more prone to limit sectors that affect the nitrogen cycle with fertilizers and chemical manufacturing and be more lenient towards livestock, mining, and waste treatment which are methane intensive industries.

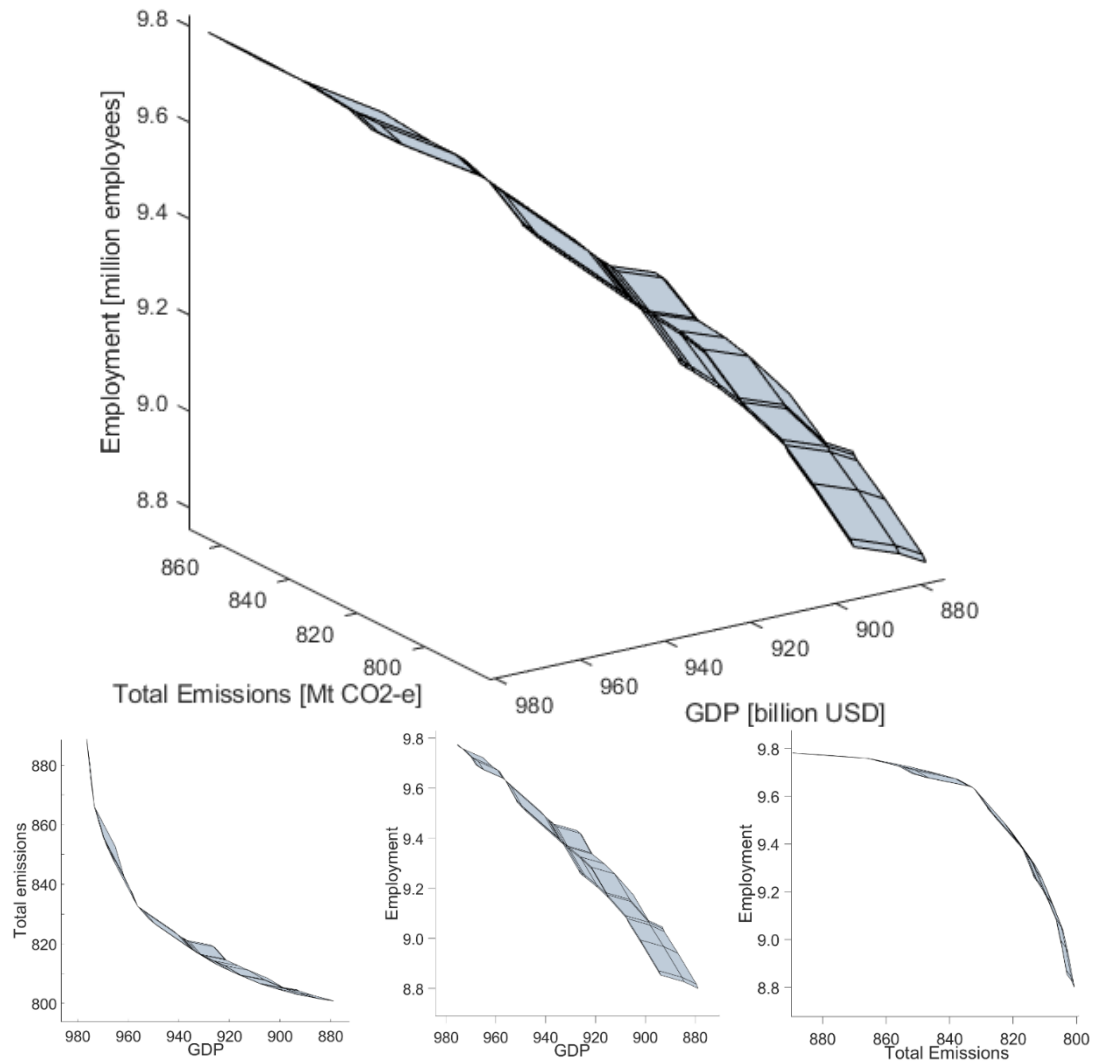


Fig. 3.9 3-D representation of optimal solution polyhedron with 2-D projections. Vertices and lines are optimal points; grey surfaces are areas of weakly efficient points

### 3.3.6 Discussion

The implication of selecting a particular constraint on consumption lies on the magnitude of reduction through the objectives involved, but it will not change the slope of the segments on the curve or readjust the hierarchy of the sectors. If the satisfaction ratio ( $\alpha$ ) would have been lower than the one used in this analysis, cuts in demand would have been allowed at a greater percentage than 10%. The segments between sectors would then be longer and each accomplished reduction in emissions would be

larger. However, the order of the sectors to cut is preserved. Therefore, the value selected for the satisfaction ratio is qualitatively trivial. The given optimal hierarchy is useful in presenting the most suitable sectors to modify consumption, regardless of the magnitude of constraint allowed.

The results of the optimisation and their plots serve as descriptive Pareto curves to determine the ordered efficiency of sectors to limit final consumption. The results do not encourage the full cut on demand upon all sectors. Such a scenario would not only be realistically unviable, but also inefficient towards the intended purpose: reduce GHG emissions with the minimum socio-economic repercussion. Hence, the model is an aid to assess the magnitude of the consequences of limiting final consumption on every sector. Subsequent additional criteria will then narrow on a possible area of focus from the most suitable sectors in the optimisation.

Moreover, particular sectors may be difficult to cut in demand because of their necessity or their linked attributes. Demand of the food sector can scarcely be limited because of growing population needs. Specifically for Australia, as Wood and Dey (2009) discussed, agriculture and mining are emissions-intensive industries that are heavily tied to employment and economic sustenance. Reluctance to cut production on such sectors reintroduces the unreliable dependence on efficiency improvements to reduce emissions. Their considerable carbon footprint should instead incentivise further scrutiny towards substitute consumption or policy-making.

This model performs the analysis and optimisation through the domestic economic flows of a regional economy without accounting explicitly for trade. Therefore, the multipliers presented may underestimate the true global emission levels that include emissions embodied in imports. Final demand of imports in 2009 Australia was, however, less than 1% of domestic final demand (including exports). Notwithstanding inaccuracies, the methodology is an effectively simple approach to



analyse key areas of focus in the economy. Further studies able to determine all embodied emissions in trade can ascertain the suitability of the preselected sectors.

Moreover, a more robust analysis that intends to quantify accurately the consequences of reducing consumption would benefit from estimating the associated rebound effect. The methodology presented is limited in that it does not model the shift in consumption patterns after regulation and its associated environmental toll. Innovative analytical methodologies –such as the one proposed by Freire-González (2017)– can be used to improve the model and estimate these behavioural repercussions, which are elemental to sustainable consumption assessments (Hertwich & Katzmayer 2003).

As it is the nature of all IO analysis, the model has limitations, such as having static linear coefficients and being unable to account for new technology or efficiency improvements. The results obtained are only as reliable and accurate as the data used. Therefore, it is paramount that IO tables are continuously updated in their economic, environmental, and social accounts. Only with recent data can coefficients used in the model reflect the true composition of the economy, providing accurate results and valuable conclusions.

### 3.4 Conclusions

This chapter has presented a descriptive analysis of a regional economy through an extended IOA model, providing a categorisation of its sectors according to GHG emissions and socio-economic multipliers. The descriptive approach discerns between emission inventories of production activities and embodied emissions of consumption patterns, thus assigning a different responsibility to the carbon footprint of industrial activities. Moreover, a MOO framework was created to map a path of reduction that considers pertinent parameters. By maximising GDP and minimising GHG emissions,

the optimal solution indicated a clear order of sectors that would need to be limited to ensure a minimal economic loss by a reduction in emissions. By further including maximisation of employment as an objective, the solution set presents available optimal scenarios to be chosen according to all available criteria. The multipliers and optimisation results indicate key sectors to limit or modify consumption in an effort to reduce GHG with minimal socio-economic impact.

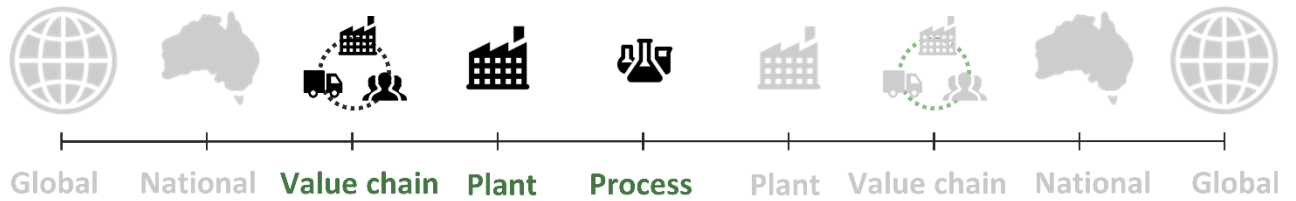
The metric for environmental impact assessments used in an analysis of this kind is of the utmost importance, since it will be the first criterion in the production of results. Exhaustive care must be put into choosing a particular characterisation value and understanding its influence in the conclusions obtained. The GWP in this methodology is based on impacts at a shorter time horizon than usual with all measured indirect effects, in an effort to reduce uncertainty and to quantify environmental consequences at the same span that measures against them should be taken. Notwithstanding the universally accepted values of GWP, there is still much uncertainty in their correctness. Hopefully, future studies will either reduce these uncertainties, making it possible to involve other gases, or consolidate other impact assessments such as GTP, which could prove to be even more useful in the guidelines of present-day environmental targets such as those of the Paris Agreement.

The results applied for the case study of the Australian economy identified the characteristics of its structure and its particular optimal reduction scheme. A preliminary analysis showed that highly intensive production sectors are not necessarily the most pollutant in terms of GHG emissions, nor do they share the same influence over GDP or employment levels. At the same time, the influence of a sector differs radically on a producer-based or on a consumer-based perspective. The true responsibility of emissions proves to be relative to the analytical lens used, creating a much more homogenous contribution of each sector to GHG emissions when a consumer perspective is adopted.

Indices helped categorise sectors according to the allocation of emissions in their output, providing an insight into the emissions structure of the economy. Australia has high GHG intensive sectors of which many other sectors rely on for their activities, showing a substantial difference in the allocation of emissions through a producer/consumer perspective. Through the optimisation, all possible emission reductions are paired to minimising economic or employment losses, presenting a map of potential solutions to meet with the areas of interest needed in the national agenda.

The model created can serve as a basis for tailored analysis in future studies. Its scalable framework allows for simultaneous multiple parameters to be included as objectives. An extended optimisation could produce robust, albeit visually inconceivable, solution spaces where a wide variety of socio-economic factors and environmental impacts are considered at once. This could help decision makers to support particular measures and identify useful policies to regulate environmental stressors. Also, the analysis presented can quickly help identify key areas of interest in an economy that could benefit from deeper scrutiny in attempting to reduce environmental impacts from modifications or regulations to their consumption. Specifically for the case study of the Australian economy, the two sectors with most potential for GHG emissions reduction with least socio-economic impact are “Agriculture, Forestry, and Fishing” and “Electricity, Gas, and Water Supply”, which are the basis of the analysis in the next chapter.

## 4 Methodology, life cycle assessment



Following the national analysis in the previous chapter, the framework increases the resolution of study towards the value chain of the identified optimal sectors and the specific characteristics of the CCU pathway to be selected. A suitable process is selected for further analysis in the LCA according to the overlap of the value-chains in the optimal sectors of the region and the viable large-scale CO<sub>2</sub> conversion pillars. Finally, special focus is given to the design of the CCU system incorporating the selected technology to create a viable and complete system including product separation.

This chapter presents an overview of the life cycle assessment (LCA) methodology in existing standards and guidelines, followed by particular considerations related to the evaluation of a CCU technology with a low technology readiness level. Continuing the application of the framework to the case study, the rationale behind selecting ethanol production based on the results of the input-output model is explained. An overview of ethanol and its production through the electrocatalytic reduction of CO<sub>2</sub> as a CCU alternative is presented, followed by a description of the methodology of the LCA to assess this technology. The chapter finishes with the

comprehensive process modelling employed to create the entire system with product separation.

This chapter draws partially from the content submitted in Rojas Sanchez *et al.* (2021).

## 4.1 Background

A CCU technology will be assessed to identify its carbon footprint and other potential environmental burdens. To ensure a correct quantification, an exhaustive analysis of the entire life cycle of the process should be performed (Hellweg & Canals 2014). Life cycle assessment (LCA) is a key tool for this endeavour.

The following section does not intend to be a full account on the methodology or mathematical basis of conducting an LCA. It provides a general overview and then focuses on select aspects of the methodology that are relevant to CCU and the proposed framework in this research.

### 4.1.1 Life cycle assessment

An LCA analyses the interaction amongst flows in the life cycle stages of a process or product to quantify its associated potential environmental impacts (von der Assen et al. 2014). Generally, the analysis ranges from the extraction of raw materials (cradle) for manufacturing up to the end use and disposal of wastes (grave). While the concept of life cycle evaluation dates back to the 1950's, it was first developed only for cost-functionality analysis in the US government (Novick 1959). The introduction of an environmental nature was developed mostly through the private sector up to the late eighties, until the establishment of a formal framework by the Society of Environmental Toxicology and Chemistry (SETAC) (Klöpffer 2006). The International Standards

Organisation (ISO) published the first standardisation of LCA practice through their 14040 series, first in 1997 and the latest version in 2006 (Guinée et al. 2011).

These standards provide an organised framework to develop a complete LCA in the form of stages, as shown in Figure 4.1. Phase 1 postulates the question to be answered and the conditions in which the results are applicable. At this phase, the *functional unit* is selected, which is the unit of fair comparison between processes based on the function realised. Phase 2 compiles all the necessary flows to characterise the processes involved. It is by far the most time-consuming and strenuous element of an LCA, since it not only needs exhaustive data collection but also an ability to create models whenever such data is not available. As Skone *et al.* (2019) very eloquently described it:

*“The development of data for life cycle models is a time-consuming process that requires a background in science and engineering, the willingness to gather information from disparate sources and normalize it to a common basis, and the ability to translate real-world phenomena into mathematical relationships.”*

Phase 3 translates the flows of the inventory in potential environmental impacts through characterisation factors, such as the global warming potential used in the input-output analysis of Chapter 3. Finally, Phase 4 interprets the obtained results to draw conclusions, understand the limitations and uncertainties of the assessment, and recommend future work (ISO 2006a). As Figure 4.1 illustrates, Phase 4 is employed not only at the end of Phase 3, but also at every point of the assessment. This iterative nature of evaluation at all stages of the LCA ensures consistency in the goal and integrity in the compiled data and obtained results.

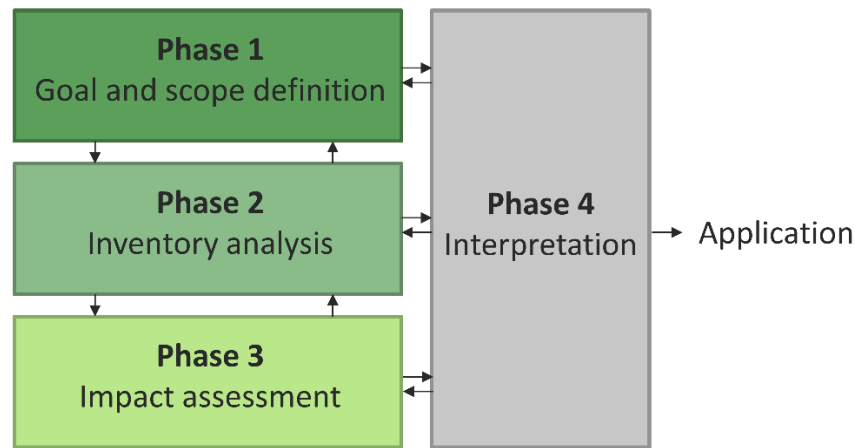


Fig. 4.1 Stages of an LCA framework as described in the ISO 14040 series

It is important to note that LCA is not able to determine the stand-alone “sustainability” of a product or process, as there is no absolute threshold. It is only able to compare its overall sustainability against a reference or the environmental impacts within its life cycle stages (Heijungs & Guinée 2012).

#### 4.1.2 Life cycle assessment for carbon capture and utilisation

The ISO standards do not consider fully the specific characteristics of CCU systems, leaving the methodology open to individual choices. This has caused a big discrepancy in LCA results, even when studying the identical process or product (Artz et al. 2018). The main areas of variation revolve on key aspects, such as the functional unit, CO<sub>2</sub> accounting, and solving the multi-functionality within the system boundary.

The characteristics of CCU systems that give rise to ambiguity, beyond those already present in general LCA studies, are the inclusion of the CO<sub>2</sub> capture process and the perspective of CO<sub>2</sub> as feedstock vs emissions reduction. CCU systems usually involve two final products: one derived from the main process and another one from the CO<sub>2</sub> capture process. The specific approach in solving this multifunctionality can lead to different results. This will be discussed in detail in the subsequent sections.

Additionally, not all assessments include the entire capture system. To illustrate, in the assessment of methanol production, Luu *et al.* (2015) excluded the

source of the CO<sub>2</sub> and simply assumed an excess amount of CO<sub>2</sub> was introduced in the system. For a similar process, Al-Kalbani *et al.* (2016) instead modelled the flue gas coming into the system and included the energy associated for its purification, but still excluded the operations from the source coal power plant. Moreover, both of these studies model the CO<sub>2</sub> flows as negative emissions (-1 kg CO<sub>2</sub>e per kg CO<sub>2</sub> captured), rather than considering it a feedstock that still incurs other associated emissions. Their approach is considerably different to that of Sternberg *et al.* (2017), which included the carbon source in the system boundaries and accounted the CO<sub>2</sub> as feedstock (-0.42 kg CO<sub>2</sub>e per kg CO<sub>2</sub> captured). Thus, the LCA practitioner is subject to making methodological choices that have led to an unhomogenised approach.

To solve this issue and ensure consistency in the elaboration of LCAs for CCU technologies, many reports and guidelines have been published (Engebø *et al.* 2014; IEAGHG 2018; Skone *et al.* 2019; von der Assen *et al.* 2014). One of the most comprehensive documents in this endeavour is the *Techno-economic assessment and life cycle assessment guidelines for CO<sub>2</sub> utilisation* by the Global CO<sub>2</sub> Initiative (Zimmermann *et al.* 2020). This report provides clear and concise directions in the formulation of the LCA. As the proposed framework in this research follows the recommendations from these guidelines, details of these are presented in the next section.

## 4.2 Modelling framework

The LCA performed adheres to the standardised methodology of ISO 14040 and 14044 (ISO 2006a, 2006b) including all necessary stages. Wherever applicable, the framework follows the recommendations of the LCA guidelines for CCU by Zimmermann *et al.* (2020). These guidelines offer a proactive approach in harmonising future studies by ensuring a consistent framework. As a new practitioner can refer to these reports for



guidance, only a few considerations from these works will be highlighted. This allows providing context for the additional considerations proposed by the present research project.

#### 4.2.1 Goal and scope definition

For the functional unit, a decision tree unambiguously indicates the recommended functional unit according to the ultimate use of the CCU technology and the identical composition of the produced molecule, as shown in Figure 4.2. Following this procedure ensures practitioners choose a consistent unit of comparison.

Additionally, when selecting the system boundaries, a cradle-to-gate approach may be sufficient for the assessment. When the composition and chemical structure of the product is identical between the CCU process and the reference, all downstream flows will also be identical. It is important to realise these system boundaries are preferable for the comparative assessment and do not quantify the potential environmental burdens of the entire life cycle of the process or product.

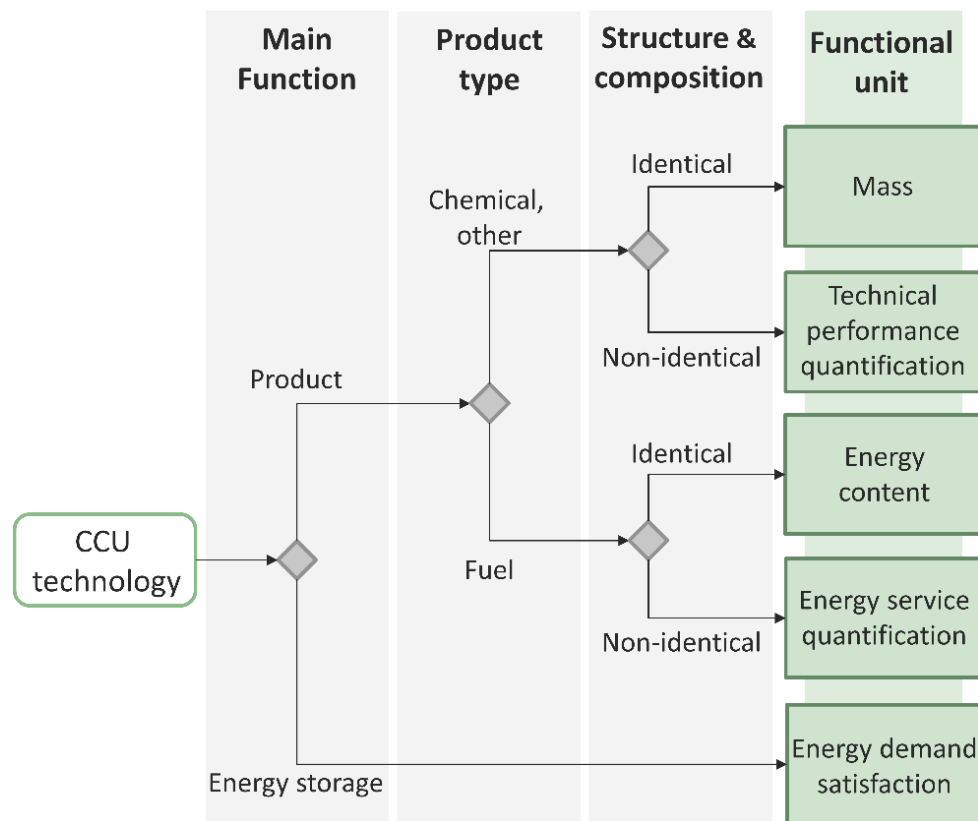


Fig. 4.2 Decision tree for selecting the functional unit of an LCA involving a CCU technology. Adapted from decision tree in Zimmerman *et al.* (2018)

As mentioned, one particular difficulty of performing an LCA on a CCU system is solving the multi-functionality of CCU systems when performing an LCA. This multi-functionality occurs when there are multiple production processes from the CO<sub>2</sub> conversion or because the source of CO<sub>2</sub> usually provides a main product (e.g. electricity from a coal power plant with post-combustion capture). As described in the guidelines and other standards (BSI 2011; European Commission 2013), the hierarchy of methods to follow to solve this is through:

1. Sub-division
2. System expansion (and substitution)
3. Allocation

Sub-division separates the system into smaller unit processes that each produce a different product to be able to discern production lines. However, applying sub-division

to CCU systems is generally impossible, since CO<sub>2</sub> is always produced together with the main product of the captured CO<sub>2</sub> source process.

Figure 4.3 shows a schematic of the different methodologies available to solve multi-functionality in CCU: system expansion, system expansion by substitution, and allocation. System expansion includes the co-product in the functional unit, and the reference will now need to include the industry standard for both products. If the increased functional unit presents a challenge in the comparison or alters significantly the goal of the LCA, system expansion by substitution may be employed. The environmental impacts of the co-production reference will then be used as a credit or offset to the CCU proposed system, representing the avoided burden. While mathematically-identical, this maintains the original functional unit for its comparison.

Finally, allocation assigns a fraction of the flows and emissions to each product in function of a specific relationship. Usually, this relationship is based on a physical attribute (such as energy content or mass proportion) or on economic value, according to what better reflects the influence of each product in the overall process (Artz et al. 2018). This method is the least recommended as it clearly presents discrepancies according to the allocation criterion selected. However, it is very commonly used in life cycle databases to describe products from multi-output plants (Wernet et al. 2017).

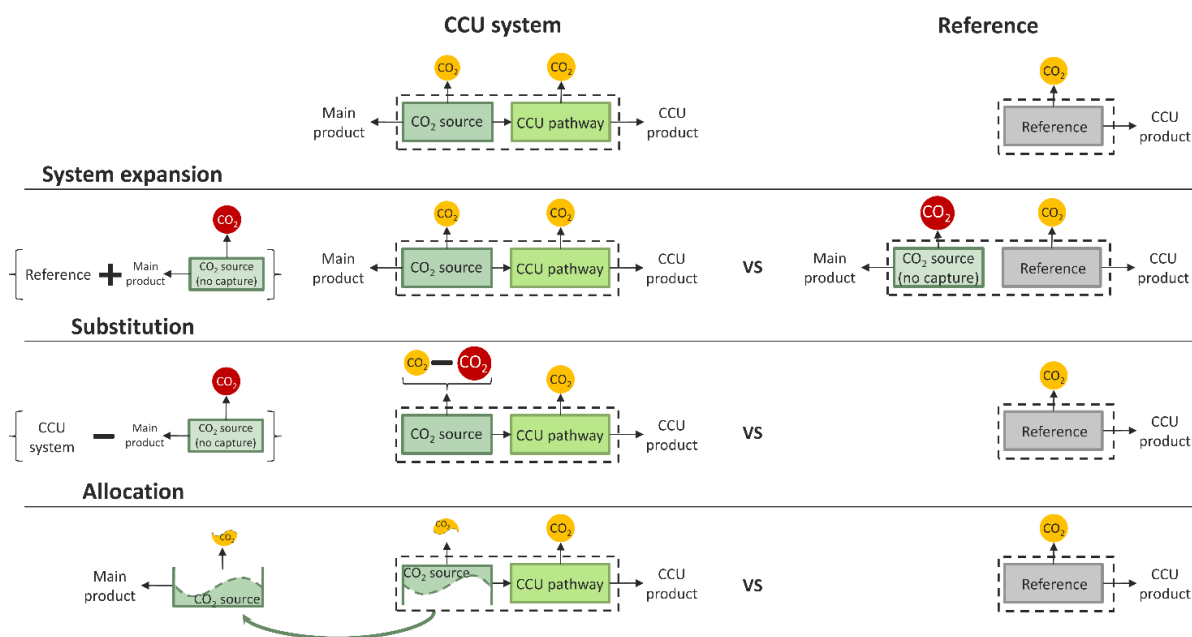


Fig. 4.3 Comparison between different methods to solve multi-functionality in CCU. System expansion, system expansion by substitution, and allocation

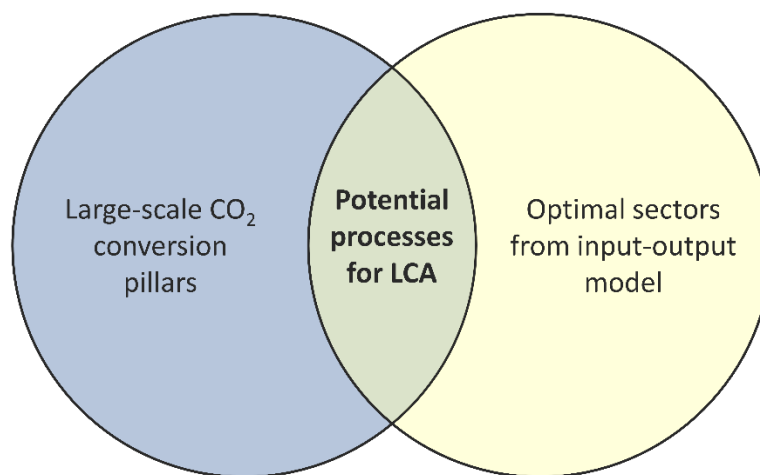
#### 4.2.1.1 CCU technology selection

Chapter 2 already provided a review of the state of the art for CCU pathways with a broad insight into readily-available and emerging technologies. Although there is a variety of very promising reaction schemes, not all of them are possible to implement on a large scale. The pathway to be selected for the future analysis must be able to be set to a scale where an impact on the reduction of CO<sub>2</sub> is substantial. Additionally, its product should also have a market demand of corresponding size. Finally, the pathway should also have a certain maturity to be able to estimate or extrapolate sufficient data for operational specifications.

The proposed framework in this research uses the cumulative insights gathered through the literature review of large-scale CO<sub>2</sub> conversion pillars and the results of the extended input-output analysis (IOA) and multi-objective optimisation (MOO) model to select the most suitable process to assess with the LCA. This process should be found from the overlap of the value-chains of the identified sectors in the model and the available opportunities of CO<sub>2</sub> conversion. Figure 4.4 highlights the need to operate

at this intersection. This is going to be specific to a region, so it is most clearly demonstrated in the case study application.

The model is able to identify the optimal sectors in the regional economy for detailed scrutiny according to the specific parameters considered in the MOO. As explained in Chapter 3, these parameters can tailor the analysis to find the most suitable area for emissions reduction in function of other socio-economic indicators.



---

Fig. 4.4 Selection of CCU potential processes for assessment in a particular region

## 4.2.2 Inventory considerations

The recommendations for data compilation used in the LCA are different according to the kind of processes in the inventory: foreground and background processes. The foreground processes are those that directly comprise the specific system to be analysed (e.g. relevant direct processes for the manufacture of a car). The background processes are the interrelated upstream processes required to facilitate the requirements of the first line of foreground processes (e.g. all associated flows in mining ore needed to create an alloy used in the manufacture of the car). As illustrated in a simple visualisation in Figure 4.5, the background processes have a complex interconnected network, while the foreground system is mainly linear with the ultimate goal of producing the functional unit.

Given its complex and extensive nature, data from background processes is generally obtained through life cycle databases. While most processes in these databases are based on generic data, some have specific data from countries or regions. Alternatively, some might have better resolution for specific processes or sectors, such as the Australian Life Cycle Initiative (AusLCI) database (Australian Life Cycle Assessment Society 2020), which has a very detailed inventory on agricultural processes for Australia. The practitioner should find the most suitable database according to the main process and location of the area of study.

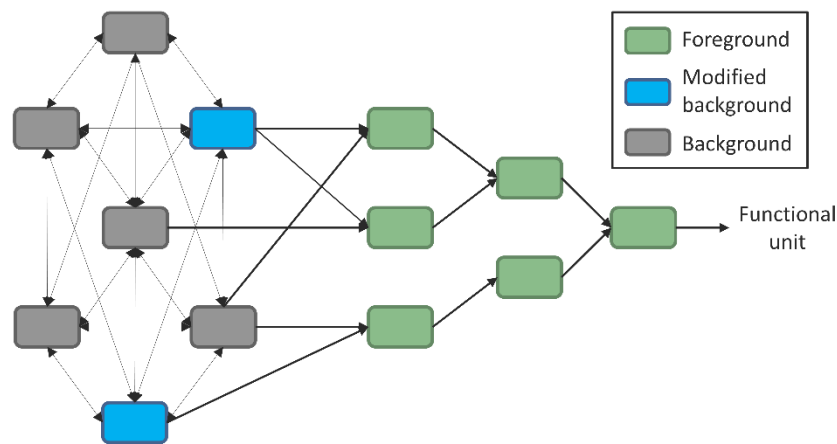


Fig. 4.5 Illustrative background and foreground processes in an LCA inventory

As seen in the illustrative inventory scheme, particular aspects of the background processes may be modified to better reflect the conditions of the specific system. Special care must be taken in such modifications, as these might affect the integrity of the original database (Wernet et al. 2016). However, when a specific process appears to have a high contribution in the overall system -generally identified after a sensitivity analysis- this should be modified with more accurate data relevant to the system. The use of LCA software, such as Simapro (PRé Consultants 2019), has an advantage for data handling and analysis.

In contrast, data from the foreground is manually compiled and is critical to the reliability of the LCA results for the examined system. These data will come from

different sources, depending on the maturity and TRL of the CCU technology. Originally developed by NASA for space programs, the TRL metric is now used universally for comparison and as a policy tool for research and innovation (EARTO, 2014). As CCU pathways generally have a low TRL and are not able to use data from plants that employ such technology, a number of considerations need to be taken to elaborate a comprehensive inventory.

#### 4.2.2.1 Considerations for low TRL CCU pathways

There is usually not enough data to assess low TRL and early-stage CCU technologies that have not been proven beyond lab scale (von der Assen 2015). Additionally, these technologies tend to have higher energy or material requirements given they have not been optimised or do not include auxiliary processes for product purification, which can have a substantial effect on the overall viability of the system (Zimmerman et al. 2018). Therefore, an engineering effort needs to be done to model this system at a relevant scale with an attempt to produce a heat or process integration. This approach provides a more complete assessment and avoids relying on oversimplified calculations for a screening assessment such as the one performed in Dutta *et al.* (2017).

A conceptual design can be proposed, based on extensive literature review from technical papers and reports, simulations, pilot plant specifications, and expert advice. A robust combination of data sources promotes the creation of a CCU system that includes all relevant auxiliary processes, which is necessary to build a realistic foreground data inventory.

It is just as important to have properly defined geographical conditions for modelling CCU systems as the background processes. Therefore, special care should be given to use assumptions and conditions specific to the region. As mentioned before, the applicability of the LCA results depend on the integrity of the data compiled in the area of study (Curran 2012).

### 4.2.3 Impact assessment methodology

The life cycle impact assessment (LCIA) methodology will also be a function of geography, both in the system boundary of the scope as in the intended area for communication of the results (European Commission - Joint Research Centre 2010). The CCU guidelines recommend the use of the CML LCIA methodology (Guinée et al. 2002), being the default for the International Environmental Product Declaration (EPD) System (Zimmermann et al. 2020). However, a number of methodologies are available for a practitioner based on European, American, international, or specialised considerations to complement the LCIA. Since the particular methodology chosen is *ad hoc*, the importance resides on the selection of the impact categories.

As the reduction of greenhouse gas emissions and reliance on fossil resources are fundamental in the use of CCU technologies, global warming and fossil resource depletion (or abiotic depletion) should be included in the assessment (Zimmermann et al. 2020). The National Energy Technology Laboratory (NETL) (Skone et al. 2019) recommends including the impact categories of the TRACI 2.1 methodology created by the Environmental Protection Agency (EPA). Although these are recommendations for LCAs for the United States, they prove to be relevant. At the same time, guidelines for specific products/processes or regions might recommend other impact categories, such as the Australian Renewable Energy Agency (ARENA) does for bioenergy products (Edge Environment & Lifecycles 2016). In the end, as Zimmermann *et al.* (2020) stated, any impact category should not be omitted if it proves to be relevant in the system and has a reliable method. Special attention should be given to the associated uncertainty in available LCIA methods.



## 4.3 Case study application

### 4.3.1 Selection of process to evaluate

According to the results of the IOA and MOO model in Chapter 3, the sectors with the highest potential to reduce emissions with the least socio-economic impact in the Australian economy are “Agriculture, Forestry, and Fishing” and “Electricity, Gas, and Water Supply”. Following the proposed methodology, the process for study should be identified in the overlap between the value-chain of these sectors and the large-scale CO<sub>2</sub> conversion pillars.

The “Electricity, Gas, and Water Supply” sector involves power and water utilities, in which the use of fuels is intrinsic. As mentioned in Chapter 2, the pillar of conversion to synthetic hydrocarbons and fuels converts CO<sub>2</sub> to oxygenated hydrocarbons that can act as fuels, such as alcohols (Quadrelli et al. 2011). From the potential alcohols, ethanol is one that is also related to the “Agriculture, Forestry, and Fishing” sector because it requires agricultural feedstock for its current industrial production. This association to agriculture further introduces water consumption and supply, strengthening the potential of ethanol as a target product in the intersection of the optimal sectors from the IO model and the large-scale CO<sub>2</sub> conversion pillars. A final criterion for the product of focus is for it to have a significant market, which will be discussed in the next section.

While bio-ethanol production through the fermentation of bio-based material is generally believed to be a clean process (Balat & Balat 2009), a CCU alternative may be able to offer benefits in global warming and other impact categories. This condition and the overlap in the interrelated value-chain of the optimal sectors identified make ethanol production a suitable process for further analysis. Moreover, ethanol production

is able to interact not only with renewable energy and CO<sub>2</sub> but also with land and water. Thus, ethanol production was selected as the process of study for the LCA.

### 4.3.2 Ethanol

While mostly used as an additive in fuel blends (Stradling et al. 2016), ethanol is also used in the manufacture of organic chemicals, personal care and cosmetics, food and beverage industries, and medical applications, among others (Zuccotti & Fabiano 2011). It has a significant market, expected to grow to US\$105 billion by 2025, mainly driven by increasing oil prices, fuel policies, and environmental concerns in the fuel industry (Global Industry Analysts Inc 2020). The industrial standard to produce ethanol is through the fermentation of bio-based material. The most common and mature pathway is through 1<sup>st</sup> generation feedstock, which are crops such as maize or sugarcane (Bruce 2013). The 2<sup>nd</sup> generation feedstocks use lignocellulosic biomass, which include residues and by-products of agricultural processes rather than the crop itself, and the emerging 3<sup>rd</sup> generation feedstock focus on the use of marine organisms such as algae ponds for the conversion (Jambo et al. 2016). Recently, the genetic modification to improve the performance of microalgae has been categorised as 4<sup>th</sup> generation biofuel production (Moravvej et al. 2019).

Although commercial progress continues to grow for 2<sup>nd</sup> generation biofuels and developments are ongoing for 3<sup>rd</sup> and 4<sup>th</sup> generation processes, 1<sup>st</sup> generation processes are still expected to dominate (OECD/FAO 2019). This brings a number of challenges, which relate to the dependence on crops and its variability with geographical and weather conditions, the use of pesticides and fertilisers (Vohra et al. 2014), water and land use (Searchinger et al. 2008), and the polemic of land for food versus fuel (Rajagopal et al. 2007). Therefore, a CCU alternative may be able to provide a promising process for ethanol production that avoids the existing disadvantages of 1<sup>st</sup> generation bioethanol production.

### 4.3.3 Ethanol production via CCU

Some of the main CCU pathways to produce ethanol include direct hydrogenation of CO<sub>2</sub> (Atsonios et al., 2016), biological conversion (Aresta et al., 2016), and electrochemical conversion. Hydrogenation is the most mature of these pathways, but it has a low selectivity to C<sub>2+</sub> alcohols (Izumi, 1997). Therefore, it has been paired with reverse water-gas shift (rWGS) to first produce carbon monoxide and then hydrogenate it to ethanol (Nieskens et al., 2011). However, the rWGS requires high temperatures, with an approximate conversion of 48% at 848K (Leonzio, 2018). It is also not able to be powered by intermittent renewable energy since the system cannot shut down and restart quickly. Ethanol can also be produced by methanol homologation or DME isomerization (Centi et al., 2013). However, in these cases, CO<sub>2</sub> would also need to first be converted to the intermediate molecule and the energy efficiency would be lower. Thus, there is a preference for direct paths to ethanol that are able to operate at ambient conditions.

Biological conversion pathways have gained attention to perform a direct conversion of CO<sub>2</sub> to alcohols by specialised microbes. Acetogenic bacteria are able to convert CO<sub>2</sub> and CO through the Wood-Ljungdahl pathway to generate a wide array of products, including ethanol (Aresta et al., 2016). Using gaseous CO<sub>2</sub> as feedstock and *Clostridium ljungdahlii*, Richter et al. (2013) produced ethanol via a two-stage system that first produced acetate and then fermented it to ethanol. However, in a recent review, Kondaveeti et al. (2020) concluded that biological technologies continue to be limited by low concentration of substrate uptake, selectivity, and productivity. Moreover, the synthesis routes for biological processes are even more staged and elaborate, increasing the complexity of the system to be paired with renewable energy and achieve industrial applications.

### 4.3.4 Electrocatalytic reduction of CO<sub>2</sub>

The electrochemical conversion or electrocatalytic reduction of CO<sub>2</sub> is a promising pathway capable of directly producing ethanol and several functionalised low-chain hydrocarbons via CO<sub>2</sub> and water. Along with mineralisation and catalytic conversion, the area of electrochemical processes currently has the highest number of CCU developers and researchers globally (Global CO<sub>2</sub> Initiative & CO<sub>2</sub> Sciences Inc. 2016).

This process promotes the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) with water in the presence of a catalyst and electricity to produce hydrogen and functionalised low-chain hydrocarbons within an electrochemical cell. This technology has the advantage of tuning the reaction rate and products by the selection of external parameters, such as the morphology of the catalyst, the electrolyte, the design of the cell, and the overpotential applied (Spinner et al. 2012). It is also capable of working efficiently at ambient conditions and with environmentally-benign electrolytes (Amos et al. 2018). When captured CO<sub>2</sub> is used in the reaction, it receives the additional benefits of being a CCU mechanism.

The major source of energy input in the electrochemical conversion of CO<sub>2</sub> is electricity, so this pathway has great potential to utilise surplus renewable energy. This electricity dependence also promotes its economic viability as it is linked to cheap renewable electricity available in the future. Moreover, the previous pathways generally require hydrogen for the conversion, which would also need to come from renewable sources. The electrochemical conversion only requires CO<sub>2</sub>, water, and electricity as the main inputs. Finally, it is also possible to be operated intermittently (Jouny et al., 2018).

Current challenges for CO<sub>2</sub>RR include reducing the overpotential to decrease energy requirements, improving the selectivity to a single product from the array of chemicals produced, and increasing the scale of the electrolyser to commercially-

relevant magnitudes (Malik et al. 2017). Nevertheless, given its potential to produce ethanol in a direct route at ambient conditions and become a renewable energy vector, the electrocatalytic reduction of CO<sub>2</sub> was chosen as the CCU pathway of focus to produce ethanol.

#### 4.3.4.1 CO<sub>2</sub>RR to ethanol

The CO<sub>2</sub>RR in an electrolyser commonly occurs in the interface between solid electrocatalyst electrodes and an aqueous solution saturated with CO<sub>2</sub> (Lim et al. 2014). While several metallic elements have the capacity to promote the CO<sub>2</sub>RR in aqueous electrolytes, only copper-based materials have recorded conversions at relevant Faradaic efficiencies (FE) towards oxygenated hydrocarbons, such as ethanol (Kuhl et al. 2012).

As this phenomenon happens on the surface of the catalyst, its microstructure is key in the rate and selectivity of the reaction (Wu et al. 2014). The addition of a co-catalyst via doping generates specific sites that promote ethanol generation, as Ren *et al.* (2016) proved by doping a Cu-based oxide electrode with zinc dopants and reporting a 29% FE at -1.05V vs RHE with a current density of 8.2mA/cm<sup>2</sup>. Carbon-based catalysts have also proven to be effective for ethanol production, with the added benefit of using low-cost and abundant materials. Song *et al.* (2016) integrated metallic and carbon-based materials to create a nitrogen-doped carbon nanospike electrode with Cu nanoparticles, achieving a FE of 63% at -1.2V vs RHE with an approximate current density of 2 mA/cm<sup>2</sup>. However, the current densities in these studies are too low, limiting its applicability within lab scale.

Recently, integrating these beneficial characteristics, Wang *et al.* (2020) developed a catalyst consisting of Cu nanoparticles with a nitrogen-doped carbon layer and a gas diffusion layer. This shortens the diffusion distance between the layer and the catalyst, thus increasing the local concentration of gaseous CO<sub>2</sub> available for

reaction. Using a flow cell reactor developed in an earlier work (Dinh et al. 2018), the catalyser was able to achieve 93% FE towards C2+ products at a current density of 300 mA/cm<sup>2</sup>, with 53% FE to ethanol at -0.68V vs RHE. To the authors' knowledge, this catalyst has the highest production rate of ethanol in the literature, considering both FE and current density. Additionally, its proved performance in a flow cell reactor makes it suitable for a scaled electrolyser system, allowing better process control and stability (Weekes et al. 2018).

### 4.3.5 Environmental assessments of CO<sub>2</sub>RR process designs

While the thermodynamics have been demonstrated and the kinetics have been studied in great detail in the literature, the analysis of practical process design and integration with CO<sub>2</sub> capture infrastructure is still required to gauge the potential of using this technology on a global scale (Chen et al. 2018). Li and Oloman (2006, 2007) designed a model for a continuous reactor to produce formate products, focusing on large-scale application and integrating relevant engineering issues for its potential industrial application. Agarwal *et al.* (2011) continued with this analysis towards large-scale formic acid production by adding a value chain analysis and identifying the viability of such a process. De Luna *et al.* (2019) did a screening analysis for ethanol, ethylene, carbon monoxide, and formic acid. Their analysis looked at technical barriers and market barriers in electrochemical production costs. However, the approach taken in this analysis overlooks the specific details of product separation, which can have a significant weight in the overall suitability of the entire system.

Only a handful of studies have performed an LCA to analyse the potential environmental impacts of an entire electrocatalytic system involving a feasible product separation. Dominguez-Ramos *et al.* (2015) assessed the global warming footprint of an electrocatalytic system based on the design by Oloman and Li (2008) to produce formic acid by using captured CO<sub>2</sub> from a coal combustion plant and sending excess

CO<sub>2</sub> to storage. This study, however, does not include a detailed simulation or modelling of the process and focuses only on greenhouse gas emissions. Later, Rumayor *et al.* (2019) increased the scope of the LCA on formic acid production to include other environmental impacts and a greater resolution on the inventory of the cell and the cathode. Nabil *et al.* (2021) then developed an LCA based on the general product separation mechanism of the previous research groups, but expanded the assessment to eight C1 and C2+ products, including ethanol. However, in order to cover the breadth of the analysis, this assessment only focuses on global warming and incorporates assumptions in electrolyser performance and product separation processes that do not reflect a detailed modelling of existing technologies. To my knowledge, an environmental assessment has not been performed for large-scale continuous ethanol production via CO<sub>2</sub>RR in detail.

#### 4.3.6 Proposed system

Thus, the proposed LCA determines the potential benefits of producing ethanol via a proposed electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system integrated with an efficient product separation design and scaled to an industrially-relevant scale. Special consideration was put in developing comprehensive inventories that reflect the entire life cycle of the processes involved. Even though the maturity of technologies with CO<sub>2</sub>RR does not meet commercialisation requirements yet (Qiao et al. 2014), this is a promising pathway that benefits from an early-stage assessment to determine potential environmental improvements against a reference process.

As mentioned in the summary, this chapter presents all the process modelling required to create the proposed ECCR system, and Chapter 5 details each phase of the entire LCA.

#### 4.3.6.1 Geographical considerations

Geographical considerations play an important role in an LCA because each point in the life cycle may be impacted by its specific environment. The scope of the analysis in the case study is based on the state of Queensland in Australia. The focus on Queensland specifically comes from economic, socio-political, and environmental reasons. The market of bioethanol is significant and expected to grow, in part because of the obligatory blending with fuel (State of Queensland 2017) and the Queensland biofutures 10-year roadmap and action plan (State of Queensland 2016), which primarily intends to increase the presence of biofuels in the state. The largest bioethanol producer in the state is Dalby Biorefinery, which uses red sorghum as feedstock. Red sorghum presents several challenges: the area where it grows is prone to severe droughts (Bryden et al. 2009), the price of sorghum has high fluctuations (Grains Research and Development Corporation 2016), and there has been a rise in exports over the years (Peters & Ward 2016). Therefore, this is a region that may support more ethanol, but may not be in a position to supply the extra demand in the same way it has done so far.

#### 4.3.7 Process modelling for proposed ECCR system

As a complete system that includes ethanol production and purification with this technology does not exist, a theoretical model was created based on one of the best performing current electrolyser designs and an innovative product separation system. It was then scaled to an industrially-relevant magnitude (Burdyny & Smith 2019). The model and its inventories were produced through data from research groups, extensive literature review, simulations, and expert advice.

The proposed ECCR system comprises a direct air capture (DAC) unit, an electrolyser stack, an adsorption unit to separate the gas products, and a distillation



unit to separate the liquid products. Figure 4.6 shows a block diagram of the process and system boundaries. The plant and its associated process consider Queensland or Australian conditions. The design of the process flowchart was inspired from Fig. 2 of the formic acid electrochemical production and separation presented by Dominguez-Ramos *et al.* (2015), where the gaseous and liquid products of the cathode are separated by adsorption and distillation.

Overall, a hierarchical methodology to process synthesis was followed: first focusing on reactions, then on separations and recycles, and then on heat integration (Smith & Linnhoff 1988). The reaction component is found in the electrolyser, which was modelled in MATLAB. The two main separations were the separation of ethylene from CO<sub>2</sub> and of ethanol from the carbonate electrolyte. The separation of ethylene in the adsorption unit was also modelled in MATLAB. The separation of ethanol in the distillation system was modelled and simulated in Aspen Plus, comprising a full heat integration. The next subsections provide a full description of each individual unit.

The specific electrolyser used in this model has a substantial co-production of ethylene, which is a highly attractive chemical with a large market. Ethylene, traditionally produced through petrochemicals, is used as a building block for a wide range of materials mainly used in packaging and end consumer markets (IHS Markit 2020). Therefore, the design of the entire system was developed with the purpose of recovering both ethanol and ethylene in high purity.

The proposed design separates the two products in the following way. Air comes in the DAC unit, supplying CO<sub>2</sub> to the gas chamber of the electrolyser stack. The reactions to products happen in both gas chamber and the cathode. Ethylene leaves as a gas and is separated in the adsorption unit, separating it from the excess CO<sub>2</sub> that is recirculated back to the electrolyser. On the liquid side, the electrolyte in the cathode is sent to the distillation unit, where the electrolyte and CO<sub>2</sub> are separated and recirculated to the electrolyser, and the ethanol is recovered.

The benchmark process, which will be explained in detail in the next chapter, is the production of bioethanol by the fermentation of red sorghum in a plant similar to the size and characteristics as Dalby Biorefinery in Queensland, Australia.

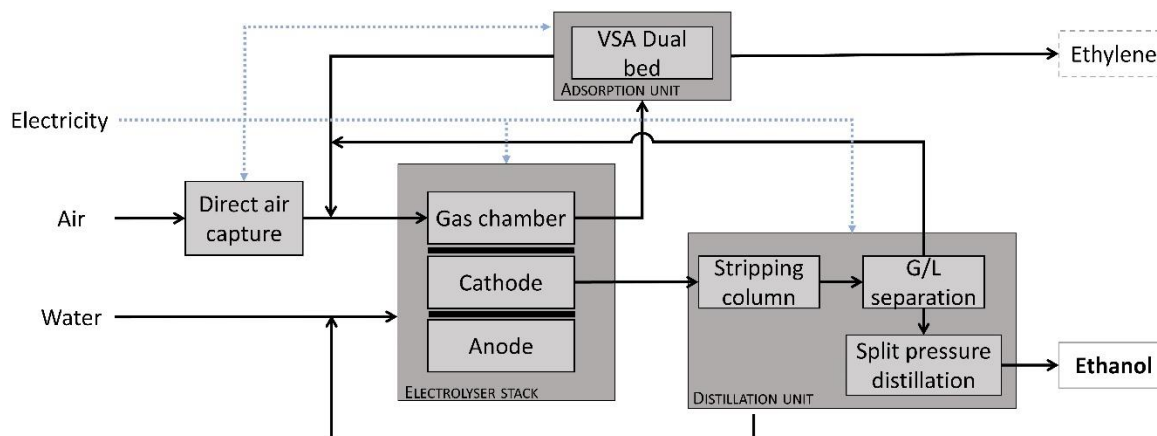


Fig. 4.6 Process flow chart of the electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system. G/L = gas/liquid. VSA = vacuum swing adsorption

#### 4.3.7.1 Direct air capture unit

The CO<sub>2</sub> is provided from DAC, as it provides a fair comparison with the benchmark agricultural process by using atmospheric CO<sub>2</sub> in both cases. The DAC process modelled was based on the process described by Keith *et al.* (2018), which is a design of Carbon Engineering Ltd. for a plant that captures approximately 1 Mt-CO<sub>2</sub> per year. It uses calcium looping with an aqueous potassium hydroxide and potassium carbonate solution in the air contactor to deliver captured CO<sub>2</sub>.

Liu *et al.* (2020) developed an LCA based on the same plant. One of the scenarios in their study included the use of an electric calciner. That same scenario was employed in this assessment, with adapted material and energy flows for the model in this paper. More information specific to this model is described in section B2 of Appendix B, while all the details of the process description can be found in the two referenced studies.

This particular DAC process was selected since it is one of the only studies to have a proposed specific design (Bui et al., 2018), it is the first to include commercial

engineering cost breakdown, and it claims to have one of the lowest associated costs: 94 USD per tonne of captured CO<sub>2</sub>. For perspective, the DAC process from Climeworks reports an approximate cost of \$600 per tonne, although they forecast a cost of \$100/tonne by 2030 (Kramer, 2018). Other DAC processes such as the one assessed by Wijesiri et al. (2019) reports \$612/tonne and the one designed by Mazzotti et al. (2013) reports \$518/tonne.

#### 4.3.7.2 Electrolyser stack

The electrolyser design is based on the experiment of Wang *et al.* (2020), using its innovative catalyst for the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) coupled with a gas diffusion layer (GDL). As first developed in a flow cell reactor by Dinh *et al.* (2018), the GDL hinders the formation of bicarbonate by only allowing a short diffusion distance between the layer and the catalyst. Tan *et al.* (2020) demonstrated that the local concentration of CO<sub>2</sub> in the active spaces of the catalyst is the main factor in producing C<sub>2</sub> hydrocarbons at high current densities. The GDL is able to promote a higher concentration of CO<sub>2</sub> available for reaction.

This catalyst has high performance and selectivity towards ethanol, which is a common challenge for electrocatalytic systems (Karamad et al. 2014). Apart from its high yield towards C<sub>2+</sub> products and the highest reported ethanol production rate, it uses relatively inexpensive materials for the catalyst and operates at ambient conditions. This reduces complexity and capital costs, allowing scale-up and stack manufacturing processes (Schmidt et al. 2017).

The electrolyser model uses the reported Faradaic efficiencies (FE) for ethanol and ethylene and assumes the remainder as hydrogen, disregarding the trace amounts of the other C<sub>1</sub> and C<sub>2+</sub> products for simplicity in the separation process. Table 4.1 summarises pertinent characteristics and performance of the electrolyser. The ambient

operating conditions of this electrolyser avoid the need for auxiliary energy and allow intermittent operation if required (Jouny et al. 2018).

Table 4.1 Characteristics of electrolyser

Parameter	Amount
Operating conditions	
Temperature [°C]	25
Pressure [atm]	1
Faradaic efficiencies	
Ethanol [%]	53
Ethylene [%]	38
Hydrogen [%]	9
KOH electrolyte concentration [M]	1
Current density [mA/cm <sup>2</sup> ]	300
Cathode	
Material	34% N/C-Cu
$E_{CO_2RR}$ [V vs RHE]	-0.68
Half-cell energy efficiency [%]	31.6
Anode	
Material	Ni foam
Full cell efficiency [%]	26.2

The electrolyte is recirculated through the cathode and anode, respectively, allowing a continuous reduced flow to the distillation system. The use of pumps and their energy requirements are considered in the assessment. The oxygen produced in the anode is assumed to vent to the atmosphere in the recirculation of the electrolyte.

The following subsection provides more information on the modelling, reactions, and rigorous carbonate equilibria calculation. Other details regarding the specific mechanism of the gas diffusion layer, the catalyst, or the flow cell reactor design can be found elsewhere (Dinh et al. 2018; X. Wang et al. 2019, 2020; Zhuang et al. 2018).

### Electrolyser model

The FE of ethanol and ethylene was taken as the reported average plus its standard deviation, with the remainder assigned to hydrogen. However, the rates of reaction and mass balance of CO<sub>2</sub> do consider the exact FE of each reported chemical, considering

its standard deviation. The FE of every product can be found in the original report (Wang et al. 2020).

Partial current densities are calculated from the FE of each reported product  $i$  and the total current density ( $j_T$ ).

$$j_i = j_T \cdot FE_i \quad (4.1)$$

The molar flowrates ( $Q_i$ ) of each product can be calculated with the electrode area ( $A$ ), the Faraday constant ( $F$ ), and the number of electrons in each reaction ( $\alpha_i$ ).

$$Q_i = \frac{j_i \cdot A}{F \cdot \alpha_i} \quad (4.2)$$

The rate of reaction or consumption of  $CO_2$  can then be derived from the molar flowrates and the stoichiometric coefficient ( $z$ ) of  $CO_2$  in the reaction of each product.

$$CO_{2RX} = \sum Q_i \cdot z_i \quad (4.3)$$

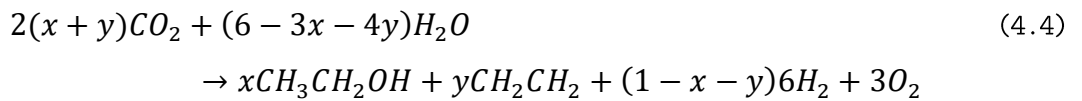
At steady-state, the flowrate of unreacted  $CO_2$  leaving the gas chamber is the difference between the inlet  $CO_2$  flowrate and the  $CO_2$  consumption reaction rate.

The main reactions occurring in both cathode and anode with their standard electrode potential at 298K are presented in Table 4.2.

Table 4.2 Main reactions in system		
	Half-cell electrochemical reactions	Potential (V vs RHE) <sup>a</sup>
Cathode	$2CO_2 + 9H_2O + 12e^- \rightarrow CH_3CH_2OH + 12OH^-$	0.09
	$2CO_2 + 8H_2O + 12e^- \rightarrow CH_2CH_2 + 12OH^-$	0.08
	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	0.00
Anode	$4OH^- \rightarrow O_2 + H_2O + 4e^-$	1.23

<sup>a</sup> Hori (2008)

By defining the FE of ethanol, ethylene, and hydrogen as  $x$ ,  $y$ , and  $1 - (x+y)$ , respectively, the global reaction can be written as,



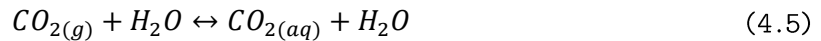
The rate of reaction of each product can then be obtained through the rate of consumption of  $CO_2$  and the stoichiometric coefficient of the global reaction. The

gaseous flowrate leaving the gas chamber of the electrolyser will be the flowrate of unreacted CO<sub>2</sub> plus the rates of reaction of ethylene and hydrogen. The electrolyte is recirculated through the cathode and anode, respectively. At steady-state, a specific composition is maintained and a reduced flowrate is continuously sent to the distillation unit.

Oxygen produced in the anode is vented through the recirculation of the anolyte in the pumping system. While there would be gaseous CO<sub>2</sub> in the anode as well, the model assumes only oxygen is vented and there are no CO<sub>2</sub> losses. The crossover of ethanol from cathode to anode is negligible with an anion exchange membrane (Ma et al. 2020). Therefore, all the ethanol produced is assumed to stay in the catholyte and arrive to the distillation system to be separated. However, all ions and CO<sub>2</sub> crossover through the membrane. Therefore, the recirculated electrolyte coming back from the distillation system that is pumped to the cathode is expected to reach equilibrium with the anolyte through the membrane. This ensures maintaining all necessary species required for the reactions in each chamber.

### Rigorous carbonate equilibria

A rigorous carbonate equilibria calculation is required to know the composition of the electrolyte that will be pumped to the distillation unit. CO<sub>2</sub> coming from the gaseous inlet to the gas chamber and crossing the GDL will continuously dissolve in the electrolyte. To determine the concentration of CO<sub>2</sub> and other carbonate species at steady-state, an equilibrium-based model was developed. The carbonate equilibria are defined by the following reactions.



According to Henry's law, the concentration of dissolved CO<sub>2</sub> can be obtained by the partial pressure of CO<sub>2</sub> in the system.

$$K_0 = \frac{[CO_{2(aq)}]}{P_{CO_2}} \quad (4.9)$$

Given the equilibrium of reaction 4.6 substantially favours the production of CO<sub>2(aq)</sub>, the equilibrium constant of the protolysis and of the hydration reaction of H<sub>2</sub>CO<sub>3</sub> is usually reported as a composite constant  $K_1$  for the joint carbonate species H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> or CO<sub>2</sub><sup>\*</sup><sub>(aq)</sub>. The concentrations of CO<sub>2(aq)</sub> and CO<sub>2</sub><sup>\*</sup><sub>(aq)</sub> are almost identical and the composite constant  $K_1$  is reported from experimental determination with higher accuracy (Stumm & Morgan 1995). This species is generally accepted as the active species for the CO<sub>2</sub>RR (Zhong et al. 2015).

The equilibrium constants are then defined as,

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_{2(aq)}^*]} \quad (4.10)$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (4.11)$$

The values of these equilibrium constants can be calculated as a function of temperature according to the parameters shown in Table 4.3.

Table 4.3 Carbonate equilibria parameters in function of temperature (T)		
pK <sub>0</sub>	-2385.73/T - 0.0152642T + 14.0184	(Harned & Davis 1943)
pK <sub>1</sub>	3404.71/T + 0.032786T - 14.8435	(Harned & Davis 1943)
pK <sub>2</sub>	2902.39/T + 0.02379T - 6.4980	(Harned & Scholes 1941)
ln K <sub>w</sub>	148.9802 - 13847.26/T - 23.6521·log(T)	(Millero 1995)

Calculating K<sub>0</sub> at ambient conditions, the maximum concentration of dissolved CO<sub>2</sub> in water is 0.0338 M. However, the CO<sub>2</sub> solubility in an electrolyte is decreased by the presence of ions in a phenomenon called the “salting-out” effect. Its effect can be quantified by the Sechenov equation:

$$\log\left(\frac{[CO_2]_{Henry}}{[CO_2]_E}\right) = K_S \cdot C_E \quad (4.12)$$

where,  $[\text{CO}_2]_{\text{Henry}}$  is the  $\text{CO}_2$  solubility in pure water,  $[\text{CO}_2]_{\text{E}}$  the solubility in the electrolyte, and  $K_S$  the Sechenov constant, which is given by the following relation.

$$K_S = \sum (h_i + h_{\text{CO}_2})n_i \quad (4.13)$$

where  $h_i$  and  $h_{\text{CO}_2}$  are the ion and gas-specific parameters for ion  $i$  and of  $\text{CO}_2$ , respectively, and  $n_i$  is the index of ion  $i$  in the formula of the salt. Given that, at steady-state, the equilibrium will convert the  $\text{KOH}$  electrolyte in  $\text{KHCO}_3$  because of the continuous input of gaseous  $\text{CO}_2$  (Blom et al. 2019), the parameters corresponding to a  $\text{KHCO}_3$  electrolyte at 298K were taken from Weisenberger and Schumpe (1996) and are shown in Table 4.4.

---

Table 4.4 Sechenov equation parameters

---

$h_{\text{K}}^+$	0.0922 $\text{m}^3 \cdot \text{kmol}^{-1}$
$h_{\text{HCO}_3^-}$	0.0967 $\text{m}^3 \cdot \text{kmol}^{-1}$
$h_{\text{CO}_2}$	-0.0172 $\text{m}^3 \cdot \text{kmol}^{-1}$

---

Therefore, the maximum concentration of  $\text{CO}_2^*_{(\text{aq})}$  in the electrolyte is 0.0237 M.

By knowing the value of  $[\text{CO}_2^*_{(\text{aq})}]$ , and adding the concentration condition,

$$C_T = [\text{CO}_2^*_{(\text{aq})}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (4.14)$$

the ion charge balance,

$$[\text{H}^+] + [\text{K}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (4.15)$$

and the dissociation of water,

$$K_w = [\text{H}^+][\text{OH}^-] \quad (4.16)$$

the system of equations (equations 4.10, 4.11, 4.14–4.16) can be solved for  $[\text{H}^+]$ . This model and system of equations were solved using MATLAB (R2020a). The concentration of all species can then be obtained, which will be the composition of the stream sent to distillation.

The solution of the system of equations gives  $[\text{H}^+] = 1.11 \times 10^{-8} \text{ M}$ , which

- by equation 4.16,  $[\text{OH}^-] = 9.12 \times 10^{-7} \text{ M}$ ;



- by equation 4.10,  $[HCO_3^-] = 9.92 \times 10^{-1} \text{ M}$ ;
- by equation 4.11,  $[CO_3^{2-}] = 4.18 \times 10^{-3} \text{ M}$ ;

The resulting concentrations are aligned to the phenomena explanation by Blom *et al.* (2019), where the KOH electrolyte is depleted by the constant flow of gaseous  $CO_2$  until it gradually becomes an  $KHCO_3$  electrolyte at equilibrium. The Sechenov relation holds for electrolytes with a salt concentration up to 5 M (Weisenberger and Schumpe, 1996).

The results of the model were compared to those reported by Gupta *et al.* (2006) for different concentrations of  $KHCO_3$  electrolyte. Figure 4.7 shows a similar pattern of the carbonate equilibria, with a slight deviation at higher concentrations. The highest discrepancy is the pH at 2 M electrolyte, with an error of 3.5%. Finally, the calculated maximum concentration of  $CO_2^*(aq)$  in the electrolyte using Sechenov relation agrees with that reported by Tan *et al.* (2020) for a 1M  $KHCO_3$  solution (23.9 mM) to within 99%.

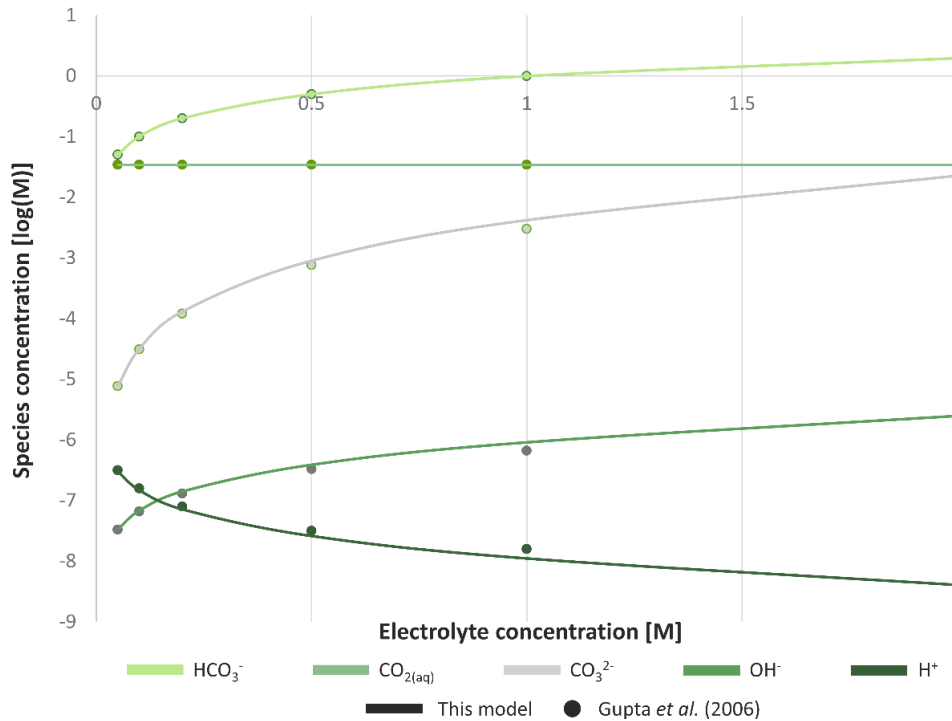


Fig. 4.7 Carbonate equilibria results validation against data reported by Gupta *et al.* (2006)

## Energy requirements

The power requirements of the electrolyser include the electricity required for the cell and the pumps to recirculate the electrolyte. The full cell potential ( $E_{\text{cell}}$ ) is the sum of the potential of the CO<sub>2</sub>RR, the oxygen evolution reaction (OER) and the overpotential of the OER. Given the overpotential for OER in Wang *et al.* (2020) was not specifically measured, an overpotential of 0.4 V was used based on the experiments on Ni foam electrodes by Liang *et al.* (2015). The power requirements (P) are then,

$$P = E_{\text{cell}} \cdot A \cdot j_T \quad (4.17)$$

The power requirements for the pumps were determined by the required head, the total volumetric flow of electrolyte, and an efficiency of 75% to maintain a conservative value.

The following additional assumptions and simplifications were considered:

- The ideal gas law holds due to the operation at atmospheric pressure
- No significant change in temperature between inputs and outputs of electrolyser due to the flow cell system
- The electrolyte recirculation was scaled-up linearly from the original design in the absence of any better information
- The inlet gas flowrate was scaled-up linearly from the original design in the absence of any better information
- The electrolyser operates at a balanced pressure in anode and cathode
- No change in performance due to fouling on either electrode
- No variations in feed
- Start-up/shutdown is instantaneous

Wang *et al.* (2020) performed a stability test with a membrane electrode assembly to identify the integrity of the catalyst. No drop on the performance was recorded in the entirety of the period. In this model, the maximum concentration of ethanol attainable in the electrolyte was determined by an assumed 10,000-minute period of continuous

operation with the same electrolyte. At steady-state, this concentration is maintained in the electrolyte and the stream that is sent for separation to the distillation unit. While this period is longer than the test of Wang *et al.* (2020), it allows building up a higher concentration of ethanol to make the separation in the distillation system more efficient. This assumption is highly conservative considering the lifetime of continuous operation in current alkaline electrolyzers (Bertuccioli et al. 2014). However, experiments have not concluded that this is the maximum operation period with the same recirculated electrolyte. Further experimentation with this electrolyser is needed to test the limits of its performance and determine the maximum operation period with the same recirculated electrolyte.

### Scaling

The proposed ECCR system was designed to produce the same output as the benchmark process. Thus, the area of the cathode was scaled to that of an advanced large-scale alkaline electrolyser, such as the one assessed by Koj *et al.* (2015). The entire electrolyser unit was then scaled-out to meet the required ethanol output by stacking assembled electrolyzers in a modular configuration working in parallel. For ease of transport and versatile installation, the electrolyser stacks were made to fit in a regular 40ft transoceanic container (GreenHydrogen.dk et al. 2016). The scaling of the required material and energy requirements for the assembled electrolyser and electrolyser stack are described in detail in Section B1.2.

#### 4.3.7.3 Adsorption system

The separation of ethylene ( $C_2H_4$ ) from the gaseous products is accomplished with a vacuum swing adsorption (VSA) unit composed of a dual bed packed with activated carbon. The selection of adsorber is based on the experiments by Zandvoort *et al.* (2020), showing an affinity for ethylene in lower concentrations in  $CO_2/C_2H_4$  containing

streams. Adsorption was preferred to other separation techniques, such as low-temperature distillation, because of the increased energy requirements and complexity due to the azeotrope between  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  (Mollerup 1975). Contrary to the original design by Dominguez-Ramos *et al.* (2015), a VSA unit is used instead of a pressure swing adsorption (PSA) unit since gases are available at atmospheric pressure. Energy consumption is reduced by only needing to recompress the adsorbed component: ethylene.

The model of the adsorption system is a simplified VSA model based on Maring and Webley (2013), using adsorption isotherms of a dual-site Langmuir model fitted for activated carbon (AC) with the experimental data of Reich *et al.* (1980). The rigorous modelling of this adsorption system is outside of the scope of this assessment.

A high purity ethylene product (99.9%) is obtained by applying a pressure swing between 0.2 bara and 1.2 bara at ambient temperature through a 13.4-minute cycle. The stream entering the adsorption unit is modelled as a binary mixture, disregarding the hydrogen ( $\text{H}_2$ ) found in low quantities that is not adsorbed by activated carbon. However, the mass balance still accounts for its fraction in the mix.  $\text{H}_2$  is not considered as a co-product in the inventory to avoid overestimating the benefits of the model. The resulting stream being recirculated to the electrolyser is composed of 99.9%  $\text{CO}_2$ . It is assumed that potential trace hydrogen impurities do not affect the performance of the electrolyser. Because of the switching work of the streams in the dual bed, shown in Figure 4.7, the bed can separate ethylene receiving a continuous input stream from the electrolyser. The following section provides more information on the modelling of this system.

### **Pre-adsorption gas recirculation**

The gas exiting the gas chamber of the electrolyser has a low concentration of ethylene (0.3%) because of the large amount of unreacted  $\text{CO}_2$ . A recirculation loop was included

at the exit of the gas chamber to increase the ethylene concentration of the stream that is sent to the adsorption system. As there is no data available for the performance of the electrolyser with products in the inlet gas stream to the gas chamber, the CO<sub>2</sub> concentration in the stream was assumed to be maintained at a minimum of 95%, allowing an ethylene concentration of 4.1% and 0.9% hydrogen. The compression work for this recirculation is low because it only has to overcome the pressure drop across the stack. However, it is included based on isentropic compression, as shown in Equation 4.18, with an efficiency of 75% and is accounted in the energy requirements of the adsorption system.

$$W = \frac{1}{\eta} \frac{kRT_{in}}{k-1} \left[ \left( \frac{P_{out}}{P_{in}} \right)^{\frac{k-1}{k}} - 1 \right] \quad (4.18)$$

#### Adsorption model for C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub>

The stream is modelled as a binary mixture given H<sub>2</sub> is not adsorbed by AC. However, the mass balance still accounts for the fraction of H<sub>2</sub> in the mix. The adsorption isotherms were calculated through the dual-site Langmuir model, described by the following expression:

$$q = q_{A,sat} \frac{b_A p}{1 + b_A p} + q_{B,sat} \frac{b_B p}{1 + b_B p} \quad (4.19)$$

With parameters  $b_A$  and  $b_B$  in function of temperature (T),

$$b_A = b_{A0} e^{\frac{E_A}{RT}}; \quad b_B = b_{B0} e^{\frac{E_B}{RT}} \quad (4.20)$$

The parameter fits were taken from Zandvoort *et al.* (2020), which were fitted through the experimental data of Reich *et al.* (1980) for AC (BPL). The fitted parameters are presented in Table 4.5.

Table 4.5 Dual-site Langmuir parameter fits for CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> in Activated Carbon

	Site A			Site B		
	q <sub>A</sub> sat [mol/kg]	b <sub>AO</sub> [Pa <sup>-1</sup> ]	E <sub>A</sub> [kJ/mol]	q <sub>B</sub> sat [mol/kg]	b <sub>BO</sub> [Pa <sup>-1</sup> ]	E <sub>B</sub> [kJ/mol]
CO <sub>2</sub>	3.5	5.62E-10	22.5	7.6	5.89E-11	22.6
C <sub>2</sub> H <sub>4</sub>	3.6	1.30E-09	24	4.4	9.63E-11	21.5

Table 4.6 indicates the conditions and properties of the bed according to the process.

Table 4.6 Properties of inlet stream and bed

Property	Amount
Temperature, T <sub>feed</sub> [K]	298.15
High operating pressure, P <sub>H</sub> [bar]	2.0
Low operating pressure, P <sub>L</sub> [bar]	0.2
Fraction of ethylene, y <sub>C<sub>2</sub>H<sub>4</sub></sub>	0.04
Fraction of CO <sub>2</sub> , y <sub>CO<sub>2</sub></sub>	0.95
Fraction of H <sub>2</sub> , y <sub>H<sub>2</sub></sub>	0.01
Bed void, ε <sub>bed</sub>	0.37 <sup>a</sup>
Density, ρ <sub>bed</sub> [kg/m <sup>3</sup> ]	480.5 <sup>a</sup>
Total void fraction, ε <sub>total</sub>	0.69 <sup>a</sup>
Heat capacity, C <sub>Ac</sub> [J/kg·K]	1050 <sup>a</sup>

<sup>a</sup> Maring and Webley (2013)

Knowing the adsorption capacity of the bed for each component is a function of its partial pressure and temperature, the difference between adsorption capacities between the high operating pressure (P<sub>H</sub>) and low operating pressure (P<sub>L</sub>) determines the working capacity (q) of the bed for each component. That amount will be desorbed alongside the gas in the void of the bed, which is the same composition as the adsorbed phase.

$$q_{C_2H_4} = f(P_{C_2H_4}, P_{CO_2}, T) \quad ; \quad q_{CO_2} = f(P_{C_2H_4}, P_{CO_2}, T) \quad (4.21)$$

$$q = f(P_H, P_L, T) \quad (4.22)$$

The mass of adsorbent was determined through the loading of ethylene in the bed, which follows the material balance,

$$q_{C_2H_4} = \frac{\dot{n}}{m_{ads}} \int_0^{t_{ss}} (y_{feed} - y_{exit}) dt \quad (4.23)$$

where  $\dot{n}$  is the total molar flowrate entering the bed,  $m_{ads}$  is the mass of the adsorbent, and  $t_{ss}$  is the time till steady-state.

The total amount of each component in the bed will be the moles adsorbed in the bed and the moles in the gas phase in the void,

$$n_i = q_i(P_i, P_j, T) \cdot m_{ads} + \frac{y_i PV}{RT} \quad (4.24)$$

Based on the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz (1965) and the transient breakthrough simulations and experiments of Zandvoort *et al.* (2020), the breakthrough of ethylene happens after that of CO<sub>2</sub>. This suggests being able to recover CO<sub>2</sub> at high purity after its breakthrough ( $t_{b,CO_2}$ ) to be recirculated to the electrolyser before ethylene breaks through ( $t_{b,C_2H_4}$ ). After saturation, the blowdown will desorb CO<sub>2</sub> more rapidly until trace amounts are only present in the exit gas, which is considered the time of depletion of CO<sub>2</sub> ( $t_{d,CO_2}$ ). At this point, the exit gas will have ethylene at high purity until the end of the blowdown cycle ( $t_c$ ).

Figure 4.8 shows a schematic of the general stages in the cycle, indicating the pressure in each bed (in bar) and the open/closed valves in each configuration. Stream A comes from the electrolyser and contains a mix of 95.0% CO<sub>2</sub>, 4.1% C<sub>2</sub>H<sub>4</sub>, and 0.9% H<sub>2</sub>. Hydrogen is assumed to flow unaltered through the bed in its entirety. Therefore, at the Saturation stage, the first bed is saturated with CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, defined by the breakthrough of C<sub>2</sub>H<sub>4</sub>. At this point, the Equalisation stage starts by closing all valves except the one between beds and reaching an equilibrium pressure of 1.1 bar between them.

The 1<sup>st</sup> Blowdown/Repressurisation stage starts by commencing the blowdown of the first bed through Stream B, which goes back to Stream A to be re-compressed and looped in the adsorption system. After the gas in the bed void blows down, CO<sub>2</sub> will be desorbed at a faster rate than the ethylene. This stream has an average composition of 97% CO<sub>2</sub> and 3% C<sub>2</sub>H<sub>4</sub>. This stream is recirculated to Stream A with

all the ethylene desorbed with the  $\text{CO}_2$  to be able to eventually separate it. Simultaneously, the second bed will now start adsorbing Stream A from the electrolyser and Stream B from the first bed, increasing its pressure. Stream C will first have  $\text{H}_2$  flowing through without having been adsorbed, and then  $\text{CO}_2$  too after its breakthrough. After all  $\text{CO}_2$  is desorbed from the first bed, the 2<sup>nd</sup> Blowdown/Feed stage begins by opening the blowdown valve now to Stream D, which will be  $\text{C}_2\text{H}_4$  in high purity. It will continue its blowdown until the breakthrough of  $\text{C}_2\text{H}_4$  is reached in the second bed. At this point, the Saturation stage is reached again in its mirrored configuration in the second bed.

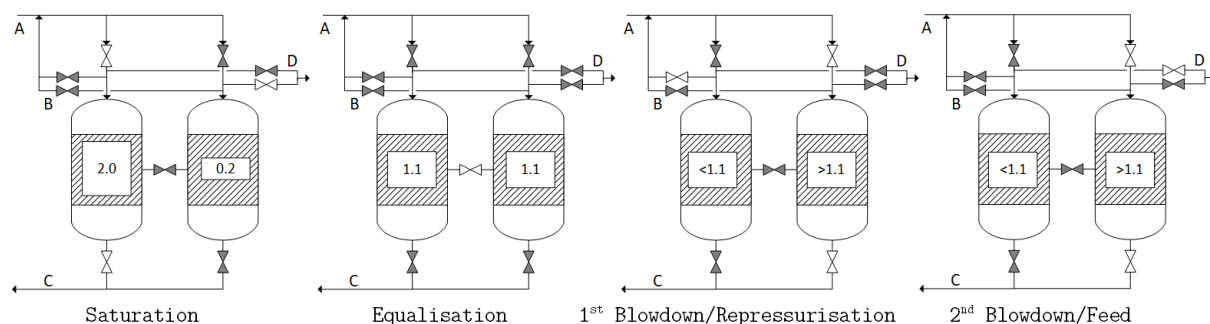


Fig. 4.8 Schematic of adsorption cycles in dual-bed system

To determine the mass balance of the entire system at steady-state, several assumptions were made. The breakthrough times were re-calculated according to the working capacity of the bed, resulting in a cycle time at cyclic steady-state ( $t_{c,ss}$ ) of 13.4 minutes. In this calculated cycle, the equalisation step is instantaneous. The trace amounts of hydrogen recirculated with the  $\text{CO}_2$  were assumed to not have an effect on the performance of the electrolyser. In case it is indeed hindered by impurities in the inlet gas stream, these trace amounts of hydrogen in Stream C exiting the blowdown before  $t_{d,\text{CO}_2}$  may be combusted before being recycled to the gas chamber. The desorption of ethylene is linear and only a function of  $t_{d,\text{CO}_2}$  to calculate the composition of this stream. The mass balance of the entire system reflects this recirculated fraction. Finally, during blowdown, the gas in the bed void is assumed to leave in its entirety.



The vacuum and blower work are calculated through isentropic compression assuming a constant isentropic efficiency of 75%. The bed is assumed to be adiabatic and isosteric heats are neglected.

The ethylene separation to pure product is 88.1% with respect to the inlet gaseous stream, with the remainder continuously looped through the adsorption system. The recirculated Stream C is virtually 100% CO<sub>2</sub> to be used as feed to the electrolyser gas chamber. As hydrogen flows through the bed before the breakthrough of CO<sub>2</sub>, a partial stream of hydrogen could be separated from the mixed stream. However, hydrogen is not considered a co-product in the inventory as it could overestimate the benefits of this theoretical and simplified adsorption model.

#### 4.3.7.4 Distillation system

Ethanol is recovered through an innovative separation system, consisting of a stripping column, heat pump, flash separator, and a split pressure distillation unit. The separation of ethanol is not simple because of the presence of dissolved CO<sub>2</sub> in the stream, increasing substantially the energy required to condense ethanol after simple distillation. The model was simulated in Aspen Plus v10 with a thermo package configured for carbonate electrolyte with a reactive chemical absorption system (Harkin 2012). A complete heat integration employing pinch analysis was developed to minimise energy requirements of the plant. The process flow diagram of the simulation is shown in Figure 4.9, which includes a highlight stream table. The full stream summary is found in Table B18.

The stripper removes most of the ethanol from the electrolyte, which is the largest component in volume. After a series of heat exchangers, the flash drum separates the lightest component, CO<sub>2</sub>, and recycles it to the electrolyser in high purity. Then the ethanol-water separation is conducted using a split pressure distillation system, which is two distillation columns operating at different pressures –low pressure

on top and high pressure in the bottom. This configuration allows using the reboiler of the low-pressure column as the condenser of the high-pressure column, reducing the utility steam and energy requirements by approximately 40% compared to using a single column. Bleeds in the three-phase condensers of both columns remove small amounts of gaseous  $\text{CO}_2$  and recirculate them upstream of the condenser. Ethanol is then condensed and recovered at the required concentration. Water is recovered from both columns and mixed with the water full of ions separated at the stripper to also be recycled as electrolyte for the cathode and anode. These recycle streams greatly reduce the amount of make-up water, electrolyte, and  $\text{CO}_2$  required for the electrolyser.

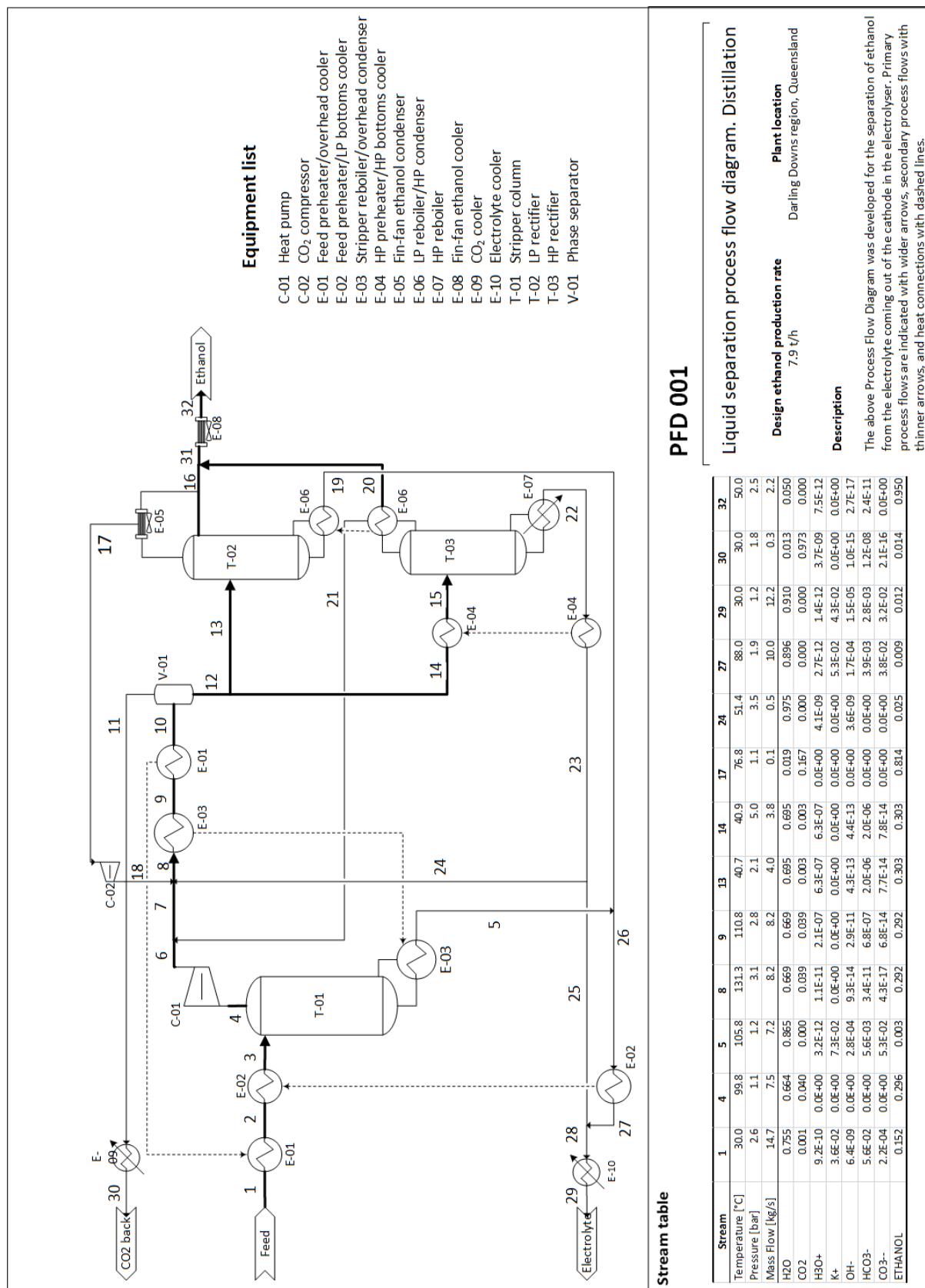


Fig. 4.9 Process flow diagram of the distillation unit simulation. Full stream table in Appendix (Table B18)

The heat integration of this separation process decreased the electricity required, achieving an energy efficiency of 92%. A critical part of the heat integration was the addition of the heat pump after the stripper (T-01). This allows the overhead vapour to be used to provide the heat for reboiling the stripper. This configuration provides a coefficient of performance (CoP) of 8.6 when considering the heat requirements saved from the condenser and the electricity penalty for the heat pump. The heat requirements of the high-pressure column are assumed to come from low pressure steam (5 bar) from an electric boiler with 95% efficiency (CIBO 2003). Therefore, all the energy requirements of the distillation unit are met with electricity. The following is a detailed explanation of the modelling and simulation.

### **Distillation model and simulation**

The model was simulated in Aspen Plus, and a complete heat integration was developed to minimise the energy requirements of the plant. Note that the following description of the process already considers the final design modifications resulting from the heat integration.

The feed stream, coming directly from the bleed of the catholyte stream in the electrolyser cell, is preheated up to a temperature of 88°C. This stream is fed to the first stage of a stripping column with no condenser (T-01). The stripping column separates 99%mol of the ethanol from the liquid mixture through the overhead stream and removing through the bottoms 75% of the water and all of the carbonate ions in solution. The overheads stream of the stripper is compressed to 3.1 bar in a heat pump (C-01), increasing the temperature of the process vapour high enough to satisfy the heat requirements of the reboiler in the stripper (E-03). The now condensed process stream is cooled to 40°C by passing through the first heat exchanger (HEX) that preheats the feed (E-01). A flash drum (V-01) then allows CO<sub>2</sub> to leave as a gaseous stream (97.4% purity, 2 bar). The liquid fraction containing water and ethanol in stream 30 is assumed to be separated and the trace amounts of gaseous water and

ethanol in the resulting stream are assumed negligible before being recirculated to the gas chamber of the electrolyser. The liquid is then divided and directed to the split pressure rectifier unit.

The split pressure rectifier unit is modelled in a similar configuration to the double-effect distillation and thermal integration by Palacios-Bereche *et al.* (2015). The unit comprises two columns, a low-pressure column (1.1 bar) and a high-pressure column (3.1 bar), which significantly reduce the energy requirements to operate them. By increasing the operating pressure of the high-pressure column (T-03), its condenser can thermodynamically satisfy the requirements of the reboiler of the low-pressure column (T-02). Because there are still considerable amounts of CO<sub>2</sub> in the top stream of the rectifiers, both columns have a three-way partial condenser, allowing a vapour bleed (79% ethanol, 17% CO<sub>2</sub>, 4% H<sub>2</sub>O) to be compressed and returned to the process upstream of the stripper reboiler process HEX (E-03). This reduces the duty required and allows both columns to distil and deliver the ethanol product at the same composition.

The bottoms of T-02 (98% water, 2% ethanol) and the stripper T-01 (carbonate solution) are mixed and then cooled down by providing the heat requirements of the second HEX that preheats the feed (E-02). The bottoms water of T-03, after preheating its own feed to bubble point, split 18% of its flow to mix with the process upstream of E-03, along with the bleeds of the rectifiers. This brings the superheated vapour process stream after the heat pump to saturation, reducing significantly the required area of the condenser/reboiler HEX. The rest of the T-03 bottoms mixes with the stream of the other bottoms, and are then cooled down back to 30°C to go back to the ECCR pump system and be used as electrolyte.

The energy efficiency of the plant is 92% (considering the energy consumed and the low heating value of ethanol in the product and in the feed), with a net power input to the system of 9.17 MW. Table 4.7 provides the duty of each heat exchanger

in the distillation system. The largest exchanger is the reboiler of the stripping column (E-03). Adding the heat pump allows using the overhead of the stripping column (T-01) to provide the heat of the reboiler. While the associated energy cost of operating the heat pump is considerable, the saving of heat duty is even greater. A coefficient of performance (CoP) of 8.57 is evidence of a good design to reduce energy requirements.

$$CoP = \frac{\text{energy saved in stripper}}{\text{energy used in heat pump}} = \frac{13.89 \text{ MW}}{1.62 \text{ MW}} = 8.57 \quad (4.25)$$

---

Table 4.7 Duty for heat exchangers in distillation unit

Heat exchanger	Duty [MW]
E-01	2.669
E-02	0.632
E-03	13.890
E-04	0.941
E-05	6.073
E-06	7.011
E-07	7.496
E-08	0.331
E-09	0.008
E-10	2.341

The recovered CO<sub>2</sub> and electrolyte are suitable to be re-used in the ECCR system, reducing the material requirements to operate the overall system. The purification of ethanol as final product is 93%, with the remainder recycled in the electrolyte continuously. The recovery of CO<sub>2</sub> is 99.9%, with a marginal loss found in the ethanol product. Because of the shifts in the carbonate equilibria during the distillation, 36% of carbonate is converted to CO<sub>2</sub> and recovered in gas form to be recirculated and used in high purity form. Because of the removal of CO<sub>2</sub>, the equilibria shift towards a higher pH and increased carbonate ions. When mixed with the necessary make-up water before entering the electrolyser once again, it has the same alkalinity and composition required to run in both cathode and anode chambers.

For the simulation, a number of assumptions were considered for the system, using the values presented in Table 4.8. The minimum temperature of utility streams

used were modelled considering geographical conditions. In the process HEX E-03 and E-06, one stream is boiling and the other is condensing. The minimum temperature approach of 5°C in these HEX is possible by using High Flux tubing, which has a high heat flux transfer area (Wisz et al. 1981). The thermo package used was previously configured for carbonate electrolyte with a reactive chemical absorption system (Harkin 2012), including the electrolyte-NRTL model for mixed solvent electrolyte system (Chen & Song 2004). The stripping column is then converged based on equilibrium.

Table 4.8 Overview of simulation assumption values

Property	Amount
Minimum temperature with cooling water	30°C
Minimum temperature with air cooling	50°C
Utility steam pressure	5 bar
Minimum temperature approach for utility and process heat exchangers	10°C
Minimum temperature approach for E-03 and E-06	5°C
Pressure drop in heat exchangers with liquid streams	0.7 bar
Pressure drop in heat exchangers with gaseous streams	0.3 bar
Isotropic efficiency of heat pump	72%

The composite curves of the final configuration of the heat integration are presented in Figure 4.10. A high integration was possible by allowing a 5°C minimum temperature difference in E-03 and E-06, indicated by the pinch point. The utility low-medium pressure steam is used to heat the reboiler of the high-pressure column T-03. Air cooling is used for the condenser of T-02 and the cooler of the product ethanol. Cooling water cools streams 29 and 30 (catholyte and CO<sub>2</sub> recycles, respectively) to 30°C. The grand composite curve is additionally shown in Figure 4.11, indicating the use of hot and cold utilities and a better visual representation of the heat recovery from the optimised configuration.

The recycling stream to be re-used as electrolyte (Stream 29) has 1.2% m/m of ethanol. To model the steady-state operation of the entire ECCR system, the electrolyser stack was re-scaled to produce the necessary amount of ethanol to arrive

to the feed concentration of 15.2% m/m of ethanol considering the composition of the recycled electrolyte. More experimentation with the selected electrolyser might prove the performance is maintained for a longer period. This would allow a higher concentration of ethanol in the catholyte, increasing its composition in the feed stream to distillation and reducing the energy requirements of the system.



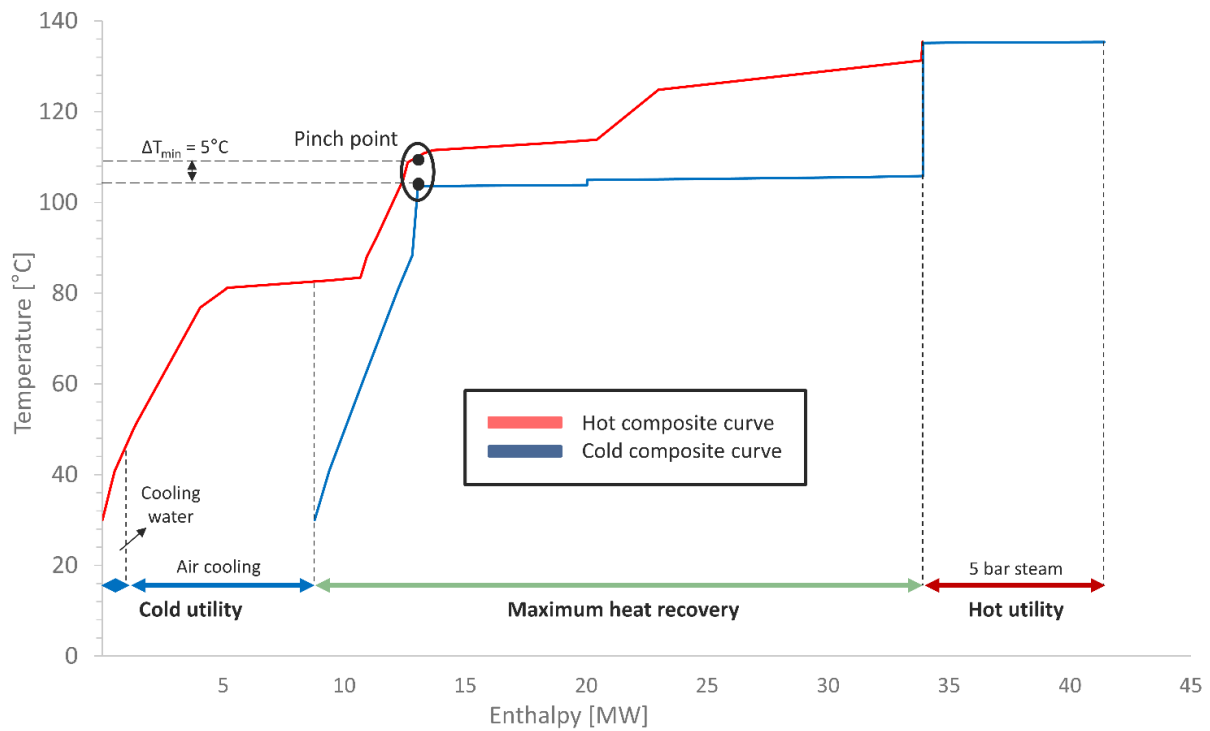


Fig. 4.10 Composite curves for the heat integration showing utilities and pinch point

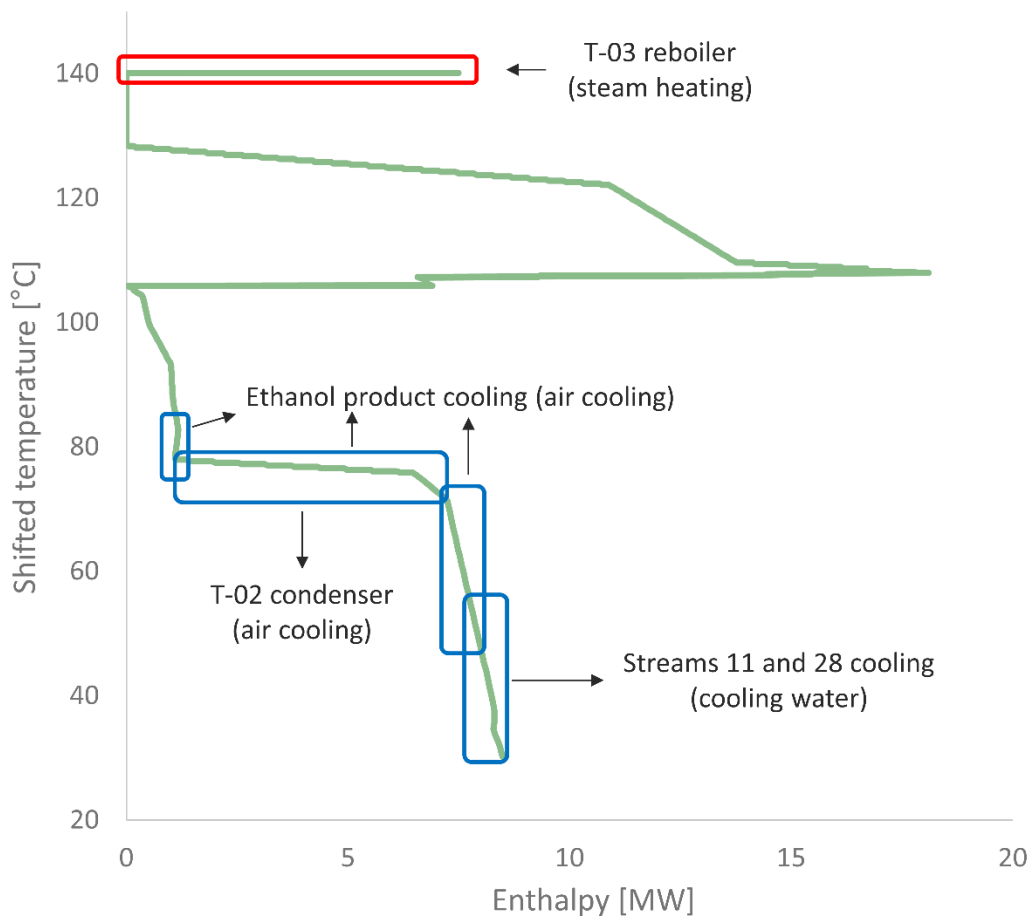


Fig. 4.11 Grand composite curve indicating required heating and cooling requirements

### 4.3.7.5 Integrated ECCR system

The entire ECCR system comprising the ECCR stack, adsorption system, and distillation system is able to operate in a continuous flow. Figure 4.12 shows the schematic of the process flow chart with the corresponding mass and energy balance. At steady-state, ethanol is produced at 2.2 kg/s and ethylene at 0.9 kg/s with a total energy requirement of 244 MW. The energy requirement to power the electrolyser itself is 213.8 MW. The extra 7 MW come from the continuous pumping of the electrolyte. Detailed information on the material and energy requirements of each unit is presented in the next chapter and in the inventories of Appendix B.

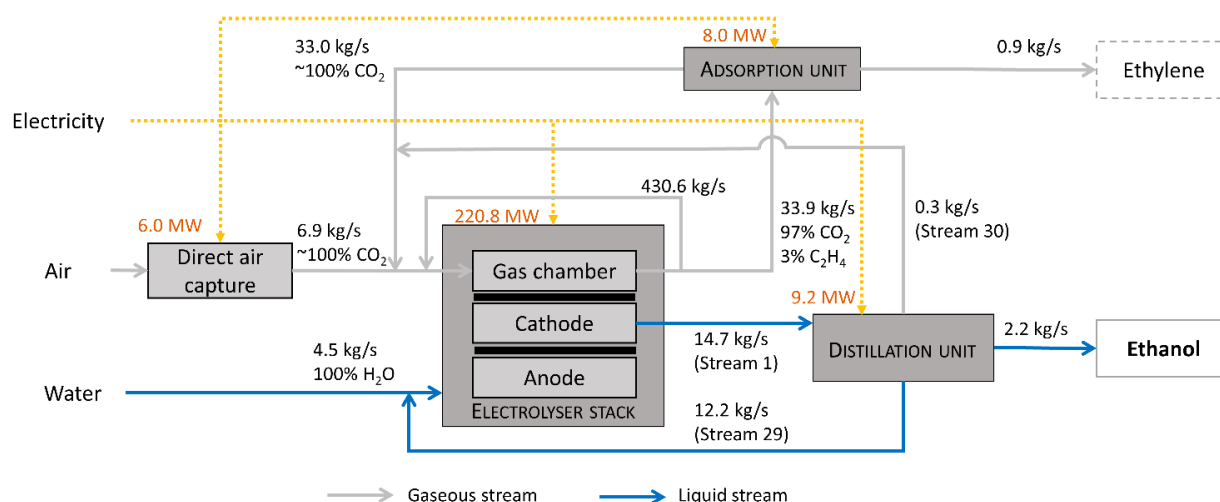


Fig. 4.12 Material and energy flows in the entire electrocatalytic captured  $\text{CO}_2$  reduction (ECCR) system

The theoretical energy requirements for the conversion of  $\text{CO}_2$  and water to ethanol (95% m/m), ethylene, hydrogen, and oxygen and their subsequent separation was calculated to be 110 MW. Thus, the energy efficiency of the entire ECCR plant is 46%. The most significant loss of efficiency comes from the overpotentials at the electrodes. The entire plant energy efficiency would increase to 55% by assuming no overpotential at the anode, and to 75% without an overpotential at the cathode. A detailed account of the theoretical energy requirements calculation is provided in section B8 of Appendix B.

The carbon balance was calculated to ensure a consistent and correct system. Table 4.9 shows the carbon balance according to all inputs to the electrolyser stack and all flows leaving the adsorption and distillation systems, including the flows that will be recirculated.

Table 4.9 Carbon balance of system including recycled streams			
Carbon in		Carbon out	
	kg/s		kg/s
CO <sub>2</sub> feed	125.16	Ethanol product	1.09
Electrolyte in	0.16	Ethylene product	0.78
		Distillation CO <sub>2</sub> recycle	0.08
		Adsorption CO <sub>2</sub> recycle	9.01
		Pre-adsorption recycle	114.20
		Electrolyte return	0.16
Total	125.32	Total	125.32

Removing recycle streams and specifying the inputs and outputs of the entire ECCR system including the DAC unit, the carbon balance is also met.

Table 4.10 Carbon balance of system with only inputs and outputs			
Carbon in		Carbon out	
	kg/s		kg/s
Captured CO <sub>2</sub>	1.87	Ethanol product	1.09
		Ethylene product	0.78
Total	1.87	Total	1.87

## 4.4 Conclusions

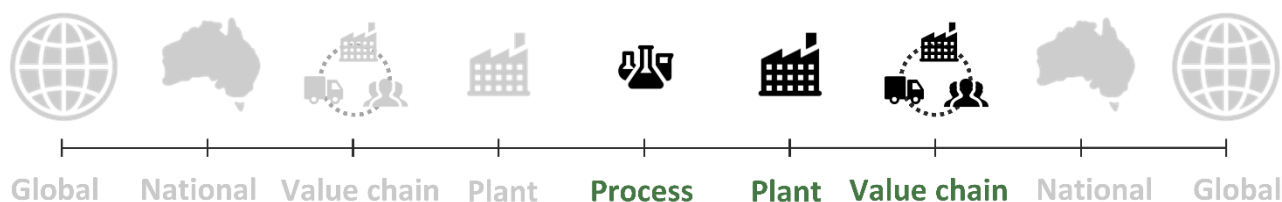
The framework proposed in this thesis considers the key parameters involved in a rigorous LCA methodology involving CCU technologies. While this methodology has been studied in detail and detailed guidelines are an aid to future practitioners, there is a considerable need for specialised engineering knowledge to develop the systems that are to be assessed. Particularly in CCU technologies with low TRL, a great number of uncertainties and unknowns arise in the elaboration of the life cycle inventory.

Therefore, the practitioner should employ comprehensive process modelling, realistic assumptions, simulations, and detailed literature review to elaborate the inventories. As in the input-output analysis, the results in an LCA are only as good as its data. As such, these should include viable product separation designs, developed by simulations and expert advice whenever there is insufficient data from commercial or pilot plants.

Regarding the case study, the chapter described the modelling of a complete system to produce ethanol through the electrochemical conversion of captured CO<sub>2</sub>. Although the current bioethanol process is considered to be sustainable from a global warming perspective, its dependence on agricultural systems, land management, and geographical conditions has sparked interest in using the electrochemical reduction of CO<sub>2</sub> as an alternative production process. The ECCR system created presents a feasible alternative that is completely independent of agricultural resources. Rigorous modelling and simulations were employed to design a realistic product separation, which is normally overlooked but can have a substantial weight on the sustainability of the entire process.

The modelling of the proposed system serves not only as an illustrative example on how to apply the framework, but also as an outlier in usual LCA comparison scope. The industry standard used as the reference system is usually a fully fossil-based pathway. However, in this case, the proposed system was designed to be compared with a bio-based reference. The next chapter demonstrates the capability of the proposed framework to identify benefits that are not initially evident.

## 5 Results, life cycle assessment



After the detailed analysis at a process level in the preceding chapter, the framework now examines the results at a processing plant level and interpret the benefits and specific considerations of the CCU technology. General recommendations are given on the presentation of the results, their visualisation, and the ease of communication to ensure the goal of the LCA is accessible.

The main content of this chapter is the application of the LCA to the case study. This LCA quantifies the potential environmental benefits of ethanol production via a proposed electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system coupled with an innovative product separation design at a commercially-relevant scale. The industry standard for bioethanol production via sorghum grain in Queensland, Australia was used as reference.

This chapter draws partially from the content submitted in Rojas Sanchez *et al.* (2021). To my knowledge, this is the first study to perform a comprehensive environmental assessment on an entire production plant using this technology to produce ethanol at a large scale.

## 5.1 LCA results considerations

In order to draw conclusions from an LCA, the results must be presented with particular considerations. Moreover, the integrity of the model should also be evaluated, and the question posed in the goal definition should be answered (Zimmermann et al. 2020). Performing a sensitivity analysis and understanding the uncertainty associated with the results is critical in this phase.

Skone *et al.* (2019) recommends that a contribution analysis be presented as a stacked bar chart to not only compare it to the reference system but also identify the areas of highest contribution to the impact within each system. Each impact category should have its own stacked chart. However, they also recommend only including the processes that have a higher than 10% contribution to the total impact, making sure to graph enough categories to show the study is complete, but not as many to prevent easy comprehension. Finally, it is important to reiterate that LCIA results are relative and do not present an absolute actual impact in the category, but rather indicate potential environmental burdens.

### 5.1.1 Uncertainty and sensitivity analysis

According to Huijbregts (1998), uncertainty is carried through the entire assessment in three ways: parameter uncertainty (e.g. imprecise measurements), model uncertainty (e.g. LCIA methodology), and uncertainty due to choices (e.g. functional unit). Therefore, sensitivity analyses are helpful in determining the associated uncertainty between the parameters used and the overall impact.

An approach to undertake a sensitivity analysis is to include scenarios to determine the worst and best-case scenarios of a key parameter of the model, delivering three discrete results to compare the system (Igos et al. 2019). As energy is a major

contribution in CCU systems, it is recommended that energy supply scenarios are constructed (Artz et al. 2018).

Another valuable method for sensitivity analysis is determining threshold values for the main parameters in the system, finding a configuration of the proposed system where a particular impact category becomes lower than the reference. As it will be illustrated in the case study application, this is especially useful when associated with the energy supplied to the system. Other stochastic methods, such as Monte Carlo simulations, are more robust methodologies to obtain a statistical result of the impacts according to the uncertainty ranges of all input variables (Williams et al. 2009).

### 5.1.2 Normalisation, weighting, and endpoint categories

The optional steps of normalisation and weighting are completely dependent on the objective and characteristics of the LCA. When accurate data for normalisation or trustworthy decision parameters for weighting are used, these might prove to be useful. While these steps can promote easier communication of results, they may not be recommended since they add a subjective layer to the evaluation (Skone et al. 2019). If they are used, the justifications and scaling criteria should be documented and the absolute indicators also presented (Zimmermann et al. 2020).

Because of the cumulative uncertainty in the methodology, the LCIA should only evaluate midpoint indicators. Although endpoint categories greatly facilitate the communication of results (especially to a non-expert audience), they carry an uncertainty that can render the results inaccurate and even draw incorrect or partial conclusions. In the same way as with normalisation and weighting, if endpoint categories are demanded by the decision-maker of the LCA, these should be carefully documented and presented with a sensitivity analysis (European Commission - Joint Research Centre 2010).

## 5.2 Case study of ethanol production via electrocatalytic reduction of captured CO<sub>2</sub>

As mentioned in the previous chapter, while CO<sub>2</sub>RR has been analysed in detail in the literature, most studies focus on the performance of the electrochemical cell without taking into account the separation process required to supply the product in its intended practical form (Ager & Lapkin 2018). Therefore, there is no clear understanding of the potential impacts of producing ethanol via ECCR at a commercially-relevant scale (Tan et al. 2020). The present study fills this gap by modelling the feasibility and potential environmental impacts of an ECCR system based on one of the best performing electrolyser designs and an innovative product separation model. This theoretical model was based on data from research groups, simulations, literature review, and expert advice.

The geographical focus of the LCA is the state of Queensland in Australia. As described in Chapter 4, Queensland presents several advantages but, above all, appears to be a region that may support more ethanol but may not be in a position to supply such extra demand in the same way it has done so far.

As the proposed framework indicates, the LCA in this study follows the standardised methodology of ISO 14040 and 14044 (ISO 2006a, 2006b), describing its stages in the subsections below. The design of the assessment follows the recommendations in the LCA guidelines for CCU by Zimmermann *et al.* (2020). The analysis was performed using Simapro version 9.0.0.48 (PRé Consultants 2019), the ecoinvent 3.5 database (Wernet et al. 2016), and the Australian Life Cycle Initiative (AusLCI) database V1.35 (Australian Life Cycle Assessment Society 2020).

In order to undertake the LCA, the following section provides the methodology, goal and scope, and description of the system. This is followed by an analysis of the



life cycle inventories and impact assessment, after which there is further discussion and conclusions.

### 5.2.1 Goal and scope

The goal of this LCA was to assess the environmental impacts of producing ethanol through the proposed ECCR system compared with the traditional fermentation of red sorghum in Queensland, Australia, to determine its suitability as a CCU pathway. The scope involved all flows associated with CO<sub>2</sub> capture, conversion, separation of products, and energy supply. Figure 5.1 illustrates the general scope. A cradle to gate approach was used for the comparison of both processes, given that the ethanol product is identical and there is no net difference between their use and disposal stages. However, the flows and emissions of the use and disposal stages of all other associated processes were considered. The functional unit is 1 kg of ethanol 95% m/m, as the product of simple distillation considering the azeotrope with water (Turner et al. 2018).

The benchmark process was based on a plant of the same size, location, and operational characteristics as Dalby Biorefinery (DB), the largest bioethanol producer in the state, producing approximately 76 ML/a of bioethanol through the fermentation of red sorghum. The process involves all flows involved in the agriculture, feedstock, and conversion systems associated with the traditional production of bioethanol (Farrell & Santella 2019).

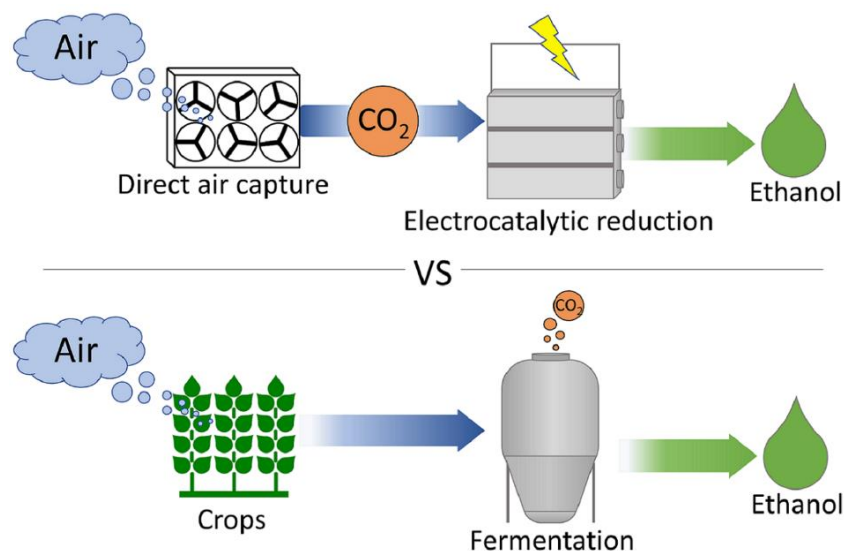


Fig. 5.1 Comparison of ethanol production via electrocatalytic captured CO<sub>2</sub> reduction (ECCR) and via the reference process of crop fermentation

As described in detail in the previous chapter, the proposed ECCR system has a direct air capture (DAC) unit, an electrolyser stack, an adsorption unit to separate the gas products, and a distillation unit to separate the liquid products. Figure 5.2 shows the block diagram of the process and system boundaries. All the information related to the modelling or description of the units in the ECCR system is found in Chapter 4.

Co-production within the system boundaries is common in CCU systems, so it needs to be solved to ensure a fair comparison to the reference system (Zimmerman et al. 2018). The LCA method used to account for this was system expansion by substitution. The associated flows and impacts of the traditional method of producing ethylene via cracking of ethane were used as credit to the impacts of the proposed CCU system. More information on this process can be found on section B4 of Appendix B. Being mathematically identical to standard system expansion, this method allows maintaining the original functional unit for comparison.

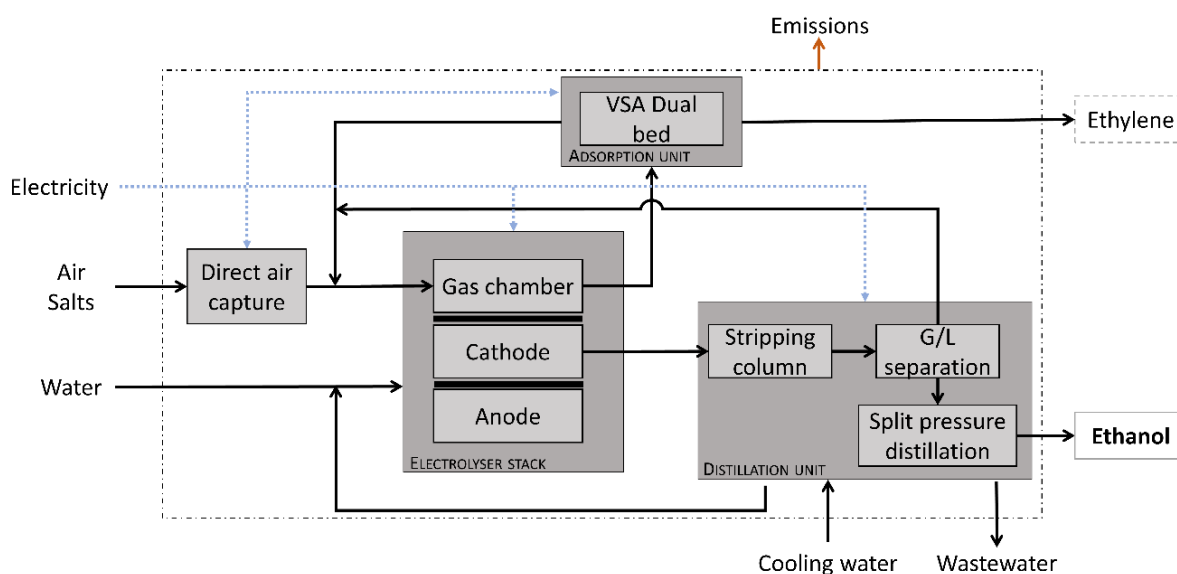


Fig. 5.2 Process flow chart and system boundaries of the electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system

## 5.2.2 Life cycle inventory and scenarios

The data for the inventories were compiled from different sources and procedures including primary data through personal communication, literature review, LCA harmonisation, process simulations, and life cycle databases. Every inventory includes material, energy and processing, infrastructure, and transport requirements, as well as direct emissions to air, water, and soil and waste outputs to treatment (and co-production when applicable). Background processes were taken from the AusLCI database, using ecoinvent processes as a proxy when processes specific to Australia or Queensland were unavailable. Commissioning and decommissioning impacts of systems, although generally disregarded for being relatively insignificant (Nabil et al. 2021), are included in this assessment for completion.

The detailed inventories, lifetimes, and assumptions of each subsystem are categorised in Appendix B. Only the final inventories of ethanol production via the ECCR system and the reference system are shown in the next subsections.

### 5.2.2.1 ECCR system

Table 5.1 shows a summary of the inventory to produce the functional unit, 1 kg of ethanol at 95% m/m. The requirements of captured CO<sub>2</sub> and softened water (for reaction in the electrolyser) consider the recirculation streams from the adsorption and distillation systems. The cooling water specified in the inventory is only the make-up water needed in the cooling tower system. The energy requirements are specified for different components of each subsystem.

The infrastructure requirements consider the equipment of each subsystem and the land occupation associated with it. For the electrolyser stack, it considers the space corresponding to the containers. For the Adsorption system, a proxy of an air separation facility process was used with the size scaled to the corresponding output. For the Distillation system, an ethanol fermentation plant process was used as a proxy, assuming 60% of the entire plant as a conservative value to consider the distillation columns in the system. The only water discharged to the wastewater treatment is the blowdown of the cooling tower.

Table 5.1 Inventory of ethanol production via the electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system. (*Details provided in Appendix section B1*)

Parameter	Amount
Functional unit output	
Ethanol production (95% m/m), by ECCR plant [kg]	1
Co-production output (avoided products)	
Ethylene, at plant [kg]	0.416
Material requirements	
Captured CO <sub>2</sub> , DAC [kg]	3.123
Water, completely softened [kg]	2.028
Cooling water [m <sup>3</sup> ]	8.51E-04
Infrastructure requirements	
ECCR stack [unit]	7.91E-10
Adsorption system [unit]	7.91E-10
Distillation system [unit]	5.00E-10
Energy and processing requirements	
Electricity, ethylene separation (adsorption system) [kWh]	0.455
Electricity, compression (pre-adsorption recirculation) [kWh]	0.555
Heat, steam (distillation system) [MJ]	3.416
Electricity, cooling water (distillation system) [kWh]	0.003
Electricity, air cooling (distillation system) [kWh]	0.004
Electricity, compressors + pumps (distillation system) [kWh]	0.207
Electricity (electrolyser) [kWh]	27.066
Electricity (electrolyte pumps) [kWh]	0.879
Waste and emissions	
Water to wastewater treatment [m <sup>3</sup> ]	1.70E-04

### 5.2.2.2 Reference production system

Figure 5.3 shows the system boundary of the reference sorghum bioethanol system. The agriculture and feedstock subsystems refer to all flows and emissions necessary for growing, transporting, and providing the sorghum grain to the plant. The conversion process to bioethanol at Dalby Biorefinery (DB) involves milling sorghum grain to a fine powder, followed by saccharification, fermentation, distillation, and dehydration through molecular sieves up to 99.5% v/v industrial grade ethanol (United Petroleum 2020). The stillage remaining after distillation is dehydrated and sold as dry distiller's

grains with solubles (DDGS), which is used as animal feed with high protein content (Bryden et al. 2009).

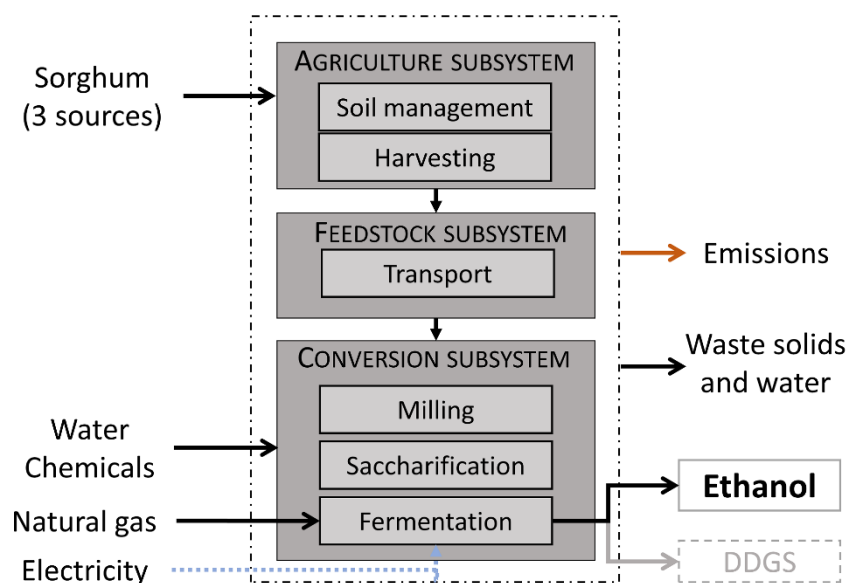


Fig. 5.3 System boundaries of the reference sorghum bioethanol system

The base inventory for the reference system was taken from an existing process in the AusLCI database modelled by allocation and based on DB-specific parameters. This inventory was compiled in high resolution through a project developed by CSIRO, the Department of Primary Industries NSW and Lifecycles for the AusLCI database (Australian Life Cycle Assessment Society 2020). The final modelled process in this assessment was modified to reflect more closely the current operation of DB and Queensland conditions (Queensland Government 2017). As Skone *et al.* (2019) detailed in the LCA guidelines by the NETL, using both system expansion by substitution and allocation within the same assessment is acceptable when allocation is constructed in detail by life cycle inventory databases. Nevertheless, Chapter 6 reproduces the results of the assessment using system expansion to solve the DDGS multifunctionality as part of the uncertainty analysis.

Table 5.2 shows the summarised unallocated inventory for sorghum bioethanol production. Sorghum is a low-yield crop available throughout the year but affected in

yield by seasonal conditions and droughts (Perez-Maldonado & Rodrigues 2009). Given a lack of data specific to DB, the origin of the sorghum feedstock was assumed to come in equal proportion from three different locations: the Darling Downs area, the Western Downs and northwest slopes and plains, and the northern zone of New South Wales. These regions are shown in Figure 5.4. All of these regions are in relatively close proximity to the plant and represent a diversity of feed throughout the year. Transport distances were averaged according to these areas.

Table 5.2 Inventory for reference sorghum bioethanol production. (*Details provided in Appendix section B5*)

Parameter	Amount
Functional unit output	
Ethanol production (95% m/m), by sorghum system [kg]	1
Material requirements	
Sorghum grain, Western Downs [kg]	1.055
Sorghum grain, Northern zone NSW [kg]	1.055
Sorghum grain, Darling Downs, QLD [kg]	1.055
Lubricating oil [kg]	2.31E-04
Water, Darling Downs [kg]	7.296
Water, completely softened [kg]	0.015
Chlorine, liquid [kg]	6.43E-06
Sodium chloride, powder [kg]	8.03E-05
Sulfuric acid [kg]	0.027
Energy and processing requirements	
Heat, natural gas, at industrial furnace [MJ]	9.482
Electricity, QLD [MJ]	0.334
Infrastructure requirements	
Occupation, industrial area [m <sup>2</sup> a]	0.087
Ethanol fermentation plant [unit]	8.33E-10
Transport requirements	
Truck, 40t [tkm]	0.633
Pipeline, natural gas [tkm]	0.036
Waste and emissions	
Carbon dioxide, biogenic [kg]	0.955
Disposal, solid waste [kg]	6.43E-05
Disposal, used mineral oil [kg]	6.43E-05
Water to wastewater treatment [m <sup>3</sup> ]	1.54E-05

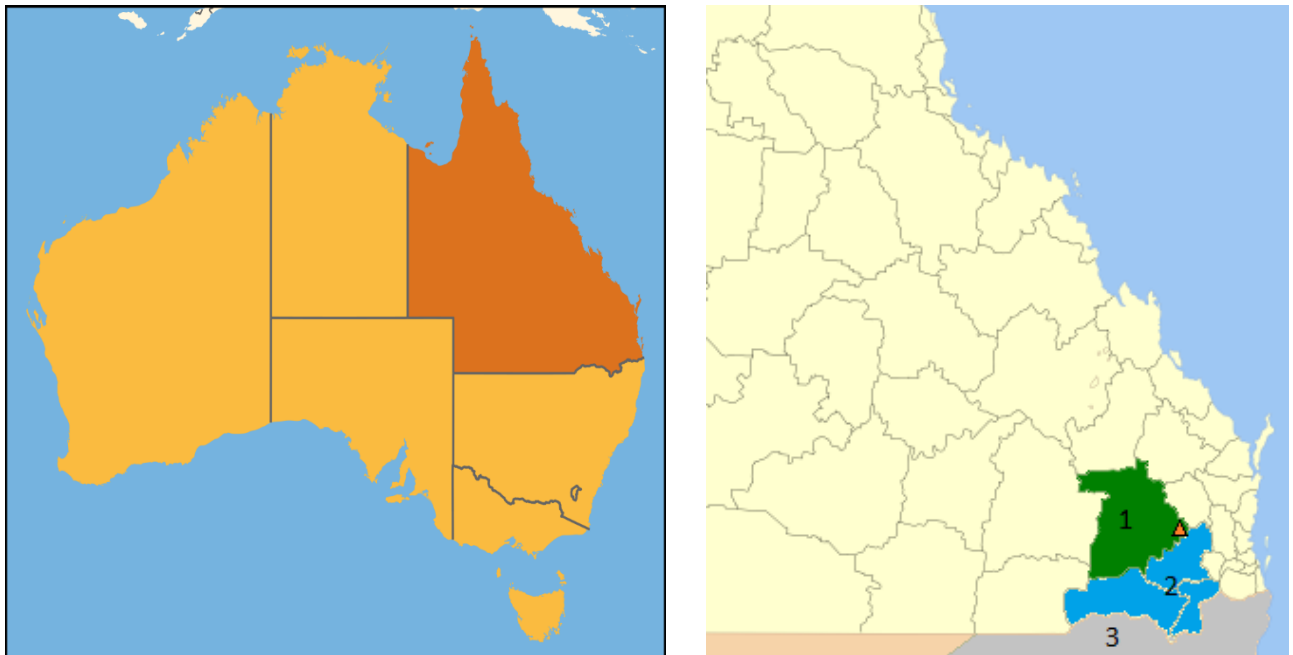


Fig. 5.4 Map of Australia with the state of Queensland highlighted (left image) and map of regions of sorghum source for Dalby Biorefinery (orange triangle): Western Downs (1, green area), Darling Downs (2, blue), and northern zone of New South Wales (3, grey) (right image). Images under Creative Commons license.

Heat requirements at DB are met with natural gas received directly at the plant through the Dalby Gas Pipeline, a connection from the Dalby Compressor Station in the Roma to Brisbane gas pipeline (United Petroleum n.d.). The electricity needed is taken from the grid. The operations at DB are typical of global bioethanol production based on crops. However, as detailed in Appendix B, the energy requirements for the usual dehydration of ethanol in the processing plant were removed from the scope to maintain the functional unit at 95% m/m. Material and energy requirements and waste treatments associated with yeast harvesting and propagation are not considered. The infrastructure requirements use the ecoinvent process for an ethanol fermentation plant scaled to the output of DB, while the area of the plot plan of the plant is specific to DB. Section B5 includes more information on the elaboration of the inventory and its assumptions.



### 5.2.2.3 Electricity input scenarios

Since the ECCR system (mainly from the operation of the electrolyser) is energy-intensive, the source of the electricity used is critical to its overall impact. Three scenarios were created (High, Mid, and Low) according to the carbon intensity of the electricity generation grid, shown in Table 5.3. The breakdown of the fuel mix in each scenario was taken from the forecasted large-scale electricity generation in Queensland for 2021, 2030, and 2050 in the latest Integrated System Plan by the Australian Energy Market Operator (AEMO) (2020a). As official projections reach 2041, the generation data for 2050 was extrapolated. The Mid scenario has a large-scale renewable energy (RE) share of 49.8%, which is consistent with Queensland’s RE target of 50% by 2030 (Queensland Renewable Energy Expert Panel 2016). The RE share for the Low scenario is 96.5%, compatible with large-scale generation in the national net-zero emissions target for 2050 (Rogelj et al. 2018). Section B1.7 shows the inventory to model high and medium voltage electricity using the grid mix scenarios.

Table 5.3 Electricity scenarios according to carbon intensity of grid by their fuel breakdown.

CCGT: combined cycle gas turbine; OCGT: Open cycle gas turbine

Scenarios				
Source	High	Mid	Low	
Black Coal	84.5%	47.0%	0.0%	
OCGT	0.0%	0.2%	0.1%	
CCGT	2.0%	3.0%	3.3%	
Hydro	1.2%	1.1%	0.2%	
Solar	8.4%	15.8%	38.6%	
Wind	3.9%	32.9%	57.8%	
Total	100.0%	100.0%	100.0%	
Renewable share	13.5%	49.8%	96.5%	
Carbon intensity [kg CO <sub>2</sub> e/kWh]	0.858	0.500	0.039	

### 5.2.3 Life cycle impact assessment

The choice of impact categories in the life cycle impact assessment is based on the recommendations by the Australian Renewable Energy Agency (ARENA) (Edge Environment & Lifecycles 2016) and the National Energy Technology Laboratory (NETL) (Skone et al. 2019) for CCU processes. The CML-IA methodology (2016, version 4.7) (J.B. Guinée et al. 2002) was used, as per the LCA guidelines for CCU (Zimmermann et al. 2020), for the following impact potentials: Global warming 100-year horizon (GWP), Acidification (AP), Eutrophication (EP), Abiotic Depletion (fossil fuels) (ADP), Ozone layer depletion (ODP), and Photochemical ozone creation (POCP). The ReCiPe methodology (Midpoint, Hierarchist, 2016, version 1.03) (Huijbregts et al. 2016) was used for Particulate matter formation potential (PMFP), Water consumption (WC), and Land use (LU).

According to the GHG accounting guidelines of the International Energy Agency (IEAGHG 2018), captured CO<sub>2</sub> from biogenic and atmospheric sources shall count as negative emissions in the inventory. Therefore, the carbon neutrality assumption for atmospheric and biogenic CO<sub>2</sub> of the Intergovernmental Panel on Climate Change (IPCC 2006) was not employed in this assessment. This comparative analysis intends to measure the flows of CO<sub>2</sub> removed from the atmosphere, regardless of their source. Therefore, the GWP accounts for the intakes and emissions of atmospheric and biogenic CO<sub>2</sub> in the flows associated to the DAC unit, fermentation, and the lifetime of the sorghum. It should be noted that the actual impact on climate change is not necessarily negative, but only a representation of the difference in carbon flows between the two systems. If the entire life cycle of ethanol is considered (e.g. combustion as a fuel), the final impact may have a positive global warming impact but would still have the same difference between the proposed system and reference.

## 5.2.4 Results

Figure 5.5 shows the potential impacts of producing the functional unit in all impact categories for the three electricity cases of the ECCR and the sorghum reference systems. Each plot is broken down in four segments with different colours. Energy represents all the energy requirements for each system. For bioethanol sorghum, it is the heat and electricity needed in the plant. For the ECCR, it is the electricity required for the electrolyser, adsorption and distillation units. Feedstock for the bioethanol sorghum is naturally sorghum with all its associated impacts. For the ECCR, it is all the embodied emissions and energy in the captured CO<sub>2</sub> from the DAC unit. The Plant category involves both commissioning and decommissioning and all the flows for the operation of the plant. Finally, grey is the ethylene credit that the ECCR system receives from its coproduction, because of the system expansion by substitution.

The ethylene credit is most evident in the abiotic depletion potential of fossil fuels (ADP), creating a marked difference between the systems. It is important to note that the ECCR does not have an actual negative flow, but is only represented as such because of the credit of ethylene. By using system expansion without substitution, the impact associated with ethylene would simply be added to the reference sorghum system. However, even when not considering the ethylene credit, the ADP of the ECCR in every scenario is comparable to the reference system. The largest contribution of the sorghum bioethanol comes from the use of natural gas (58%) for its heat requirements, followed by the use of urea (22%) for the sorghum, which needs ammonia from steam reforming and fossil fuels. For the ECCR, the largest contribution comes from the use of natural gas in combined cycle gas turbine (CCGT) electricity generation (40 – 49%).

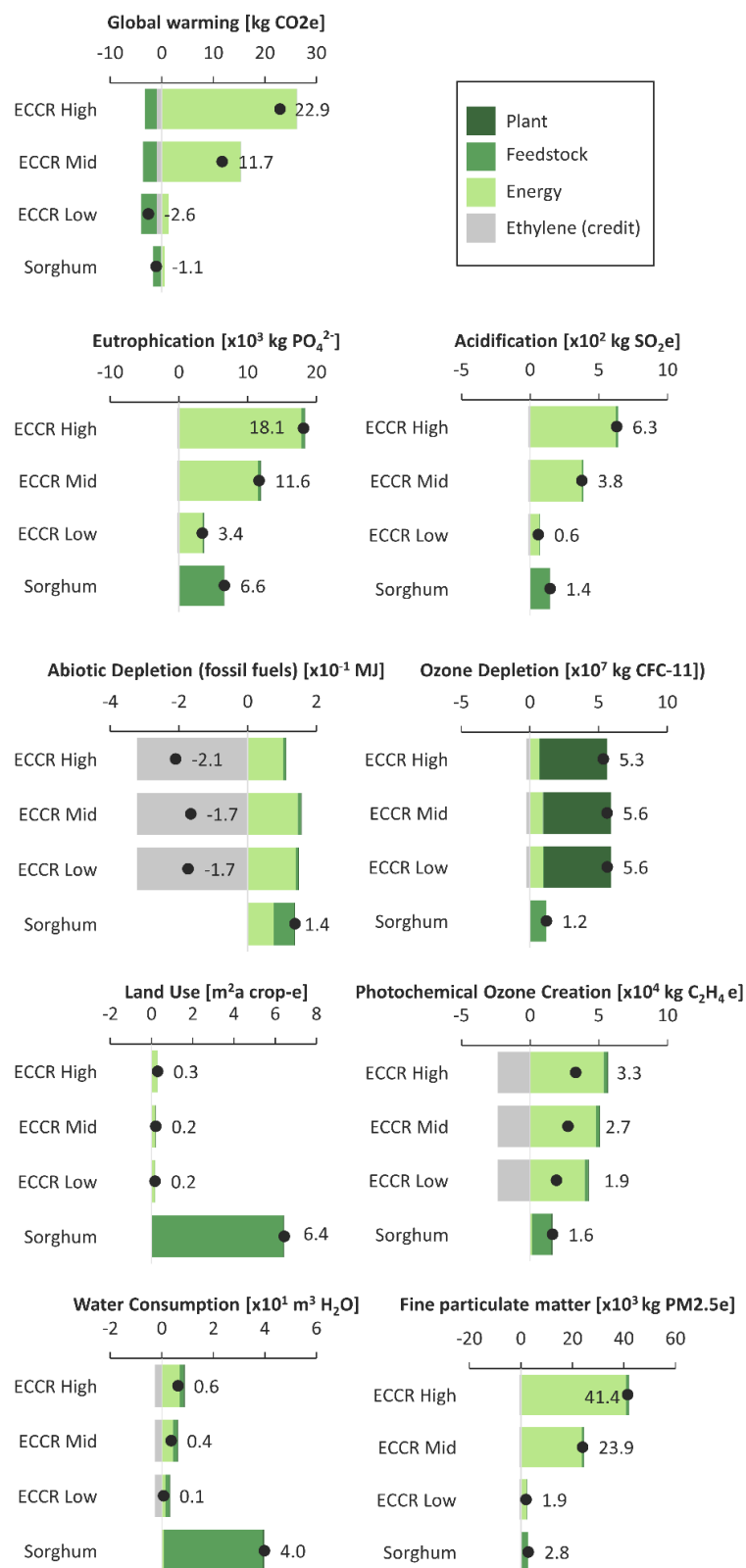


Fig. 5.5 Potential environmental impacts in all categories of the electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system at the High, Mid, and Low carbon intensity electricity scenarios and the reference system of sorghum bioethanol

In three of the nine environmental impact categories, the ECCR system at any scenario has a lower impact than the reference sorghum bioethanol. In contrast, the impact of the reference is lower than any ECCR scenario in two categories. Global warming potential (GWP), eutrophication potential (EP), acidification potential (AP), and fine particulate matter formation (FPMF) are categories where only the ECCR Low-CI scenario has a lower impact than the reference. In these four impacts, the energy supply of the ECCR has the largest contribution. Therefore, increasing the RE share of the electricity supplied decreases its impact until it is lower than the reference. For the reference system, the life cycle of the sorghum feedstock is the main contributor to most of the examined impact categories.

FPMF for the ECCR shows a direct influence on the fuel mix used. At the High-CI scenario, electricity from black coal is virtually the sole contribution to the impact (99%). In the Low-CI scenario, most of the impact comes from wind turbines construction and its required market for copper (57%) and solar electricity generation and its need for iron-nickel-chromium alloy (35%). The impact of the reference system comes mainly from the burning of the sorghum residue (61%) and the manufacture of urea (8%) and monoammonium phosphate (6%) as fertiliser.

The energy used in the ECCR is critical in reducing its associated impact. With respect to AP, the generation of electricity from black coal contributes to almost 98% of the High-CI scenario. The mining of copper for wind turbines and network connections contributes 55% of the impact in the Low-CI scenario, followed by the use of nickel in the receiver system of solar electricity generation. Similarly, black coal accounts for 96% of the impact in the High-CI scenario of EP. Sulfidic tailing associated with the copper for wind turbine network contributes 1% in the High-CI scenario to over 56% in the Low-CI scenario. In the reference system, the manufacture and leaching of chemicals in fertilisers for sorghum account for 93% and 94% of AP and EP, respectively.

The GWP of the ECCR system is mainly driven by the use of black coal in the electricity grid, substantially reduced by the captured CO<sub>2</sub> of the DAC unit and the ethylene credit. Feedstock decreases in magnitude through the electricity scenarios because of the lower CI of the energy required to capture CO<sub>2</sub>. The GWP of bioethanol sorghum coming from energy use is offset by the CO<sub>2</sub> captured by the crop during its lifetime. As the electricity mix changes, there is a breakeven between the Mid and Low-CI scenarios. To explore this pattern further, Figure 5.6 shows the GWP or carbon footprint of producing the functional unit via the ECCR system (dark blue line) and via the sorghum reference (light green line) by varying the CI of the electricity used. The grid electricity scenarios are shown in the three green circles with a corresponding H, M, and L for the High, Mid, and Low-CI scenarios, respectively. The breakeven is visible in the intersection, indicating that the ECCR system and the sorghum bioethanol reference have the same carbon footprint when the electricity used for the ECCR is 80 g CO<sub>2</sub>e/kWh.

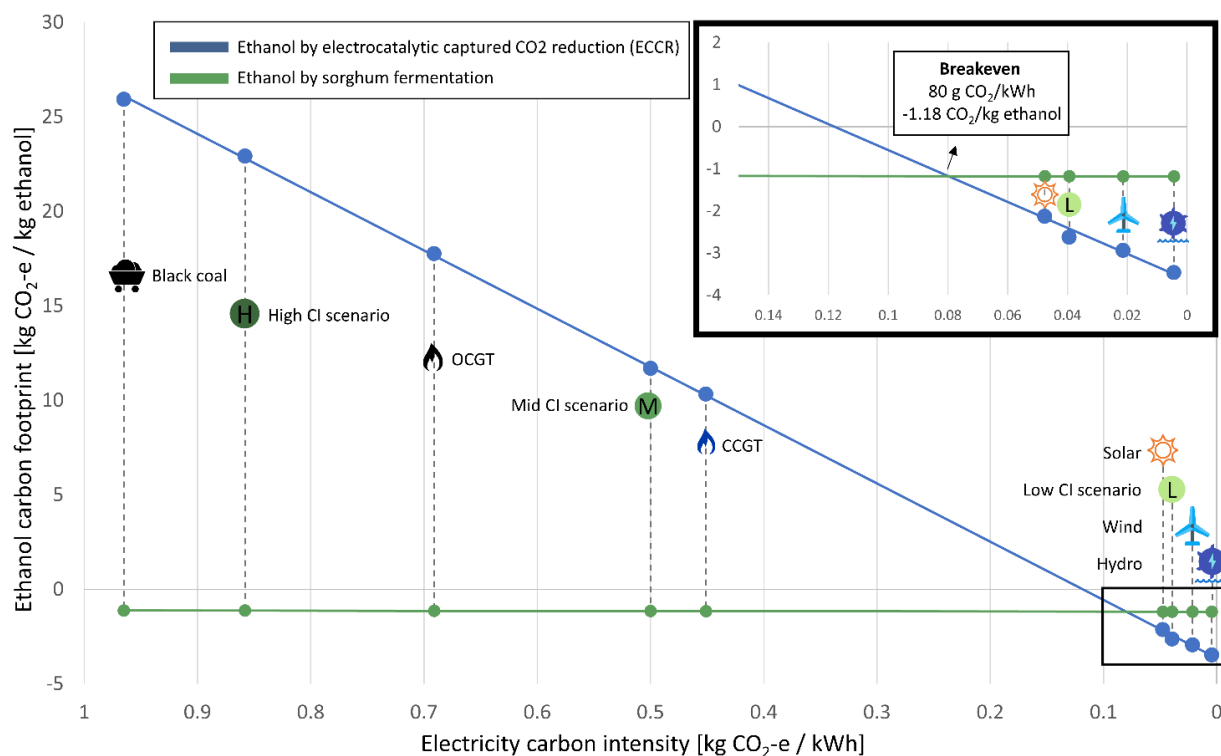


Fig. 5.6 Carbon footprint of ethanol production by the electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system (dark blue line) and by the sorghum reference (light green line) with electricity of different sources and carbon intensity. Icons taken from open-source websites icons8.com and cleanpng.com

These results imply that the ECCR system requires an electricity supply with a substantially lower carbon footprint than the current Queensland grid. However, at present day, using any source of energy that has a CI lower than that value will render the ethanol production via the ECCR system more competitive than via sorghum fermentation. The other points in the plot show the carbon footprint of ethanol production when using electricity from a single fuel type, according to its fuel emission intensity. This indicates that using a high contribution of renewable energy or employing solely one of these renewable sources provides a benefit from a global warming perspective.

The slope of the curves represents the global warming sensitivity of each process to the CI of the electricity used. The carbon footprint of the ECCR process is very sensitive to changes in the fuel mix of the energy, while sorghum bioethanol has a marginal change. The latter is not unexpected given the lower relative use of electricity

in the reference system. While the reference process could use an electric boiler instead of natural gas for its heat requirements, this is unlikely in DB because of the installed pipeline delivering natural gas straight to the biorefinery. Regardless, Figure 5.7 shows the carbon footprint sensitivity analysis for this scenario, including all three processes: ECCR, sorghum (electric), and sorghum (natural gas). It indicates that the breakeven of the all-electric reference with the ECCR system is at 70 g CO<sub>2</sub>e/kWh, which is 13% lower than the breakeven with the current natural gas-powered reference. From a GWP perspective, it would only be beneficial to use an electric boiler for the sorghum bioethanol process if the CI of the electricity supplied is lower than 225 g CO<sub>2</sub>e/kWh.

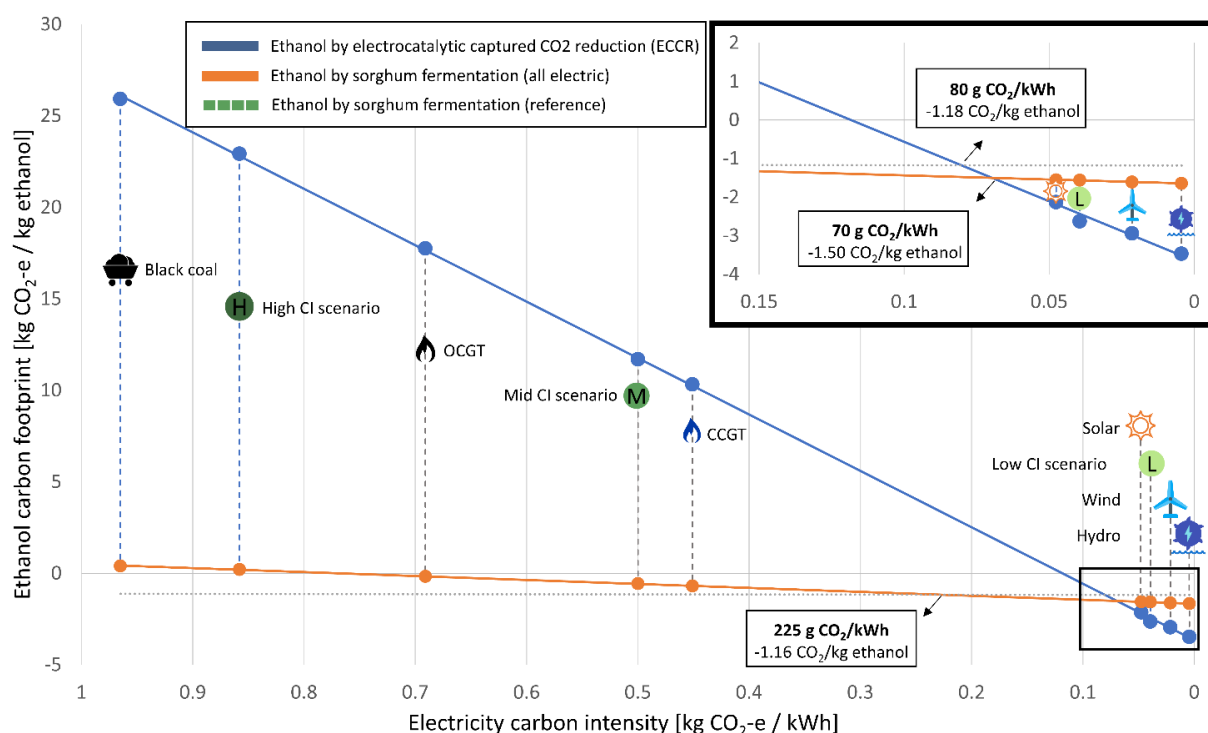


Fig. 5.7 Carbon footprint of ethanol production by ECCR (blue line), by sorghum using only electricity (orange line), and by the reference sorghum process (dotted green line) with electricity of different sources and carbon intensity. Icons taken from open-source websites icons8.com and cleanpng.com

Considering the POCP, while the impact of the ECCR Low-CI scenario is only 17% higher than the reference, the sorghum bioethanol has a lower impact than the ECCR at any scenario. At the High-CI scenario, most of the impact of the ECCR derives from the use of black coal in the electricity grid (94%). At the Low-CI scenario, the mining



for necessary metals for wind and solar electricity generation have the highest contribution, such as copper (24%), sinter iron (18%) for reinforced steel (24%), and nickel (12%). While there is no single hotspot, the summed impact of these components becomes higher than the reference because of the intensity of the energy needed for the ECCR system.

ODP is the only category where the plant component has the highest contribution, making the ECCR system have a significantly higher impact than the reference. The use of polytetrafluoroethylene (PTFE) in the cathode and assembled electrolyser represents 94-95% of the impact. This will be investigated in detail in the sensitivity analysis further in this chapter. For the reference system, the use of herbicides (11% of POCP and 68% of ODP) and urea (12% of POCP and 6% of ODP) play a major role. Monoammonium phosphate has the highest contribution in POCP (15%) and diesel for pumping water for irrigated sorghum and for the transport of feedstock account for an extra 7% in POCP and 13% in ODP.

Finally, the ECCR system at all scenarios has a considerably lower impact in water consumption (WC) and land use (LU) than the bioethanol reference. WC is an impact category of great importance because water is critical in the area of study and the bio-based benchmark requires large amounts of water. The ECCR system at its worst-case scenario uses approximately 15% of the water needed for the sorghum bioethanol reference. Its consumption lies mainly on the grid's use of black coal (38%) in the High-CI scenario, and on softened water for capturing CO<sub>2</sub> (43%) for the Low-CI scenario. For the reference system, water consumption comes almost entirely from irrigation for the irrigated sorghum.

Therefore, a sensitivity analysis was performed to explore the effects of using different combinations of sorghum sources for bioethanol production. Figure 5.8 shows the difference of WC, LU, and GWP for the production of 1 kg of sorghum bioethanol production using equal parts of the three selected regions (3 Regions), equal parts of

sorghum of dryland regions (Dryland), and only irrigated sorghum (Irrigated), with the worst and best-case scenarios for the ECCR. The dryland sources (Darling and Western Downs) have very similar impacts and were used as a single sensitivity analysis scenario.

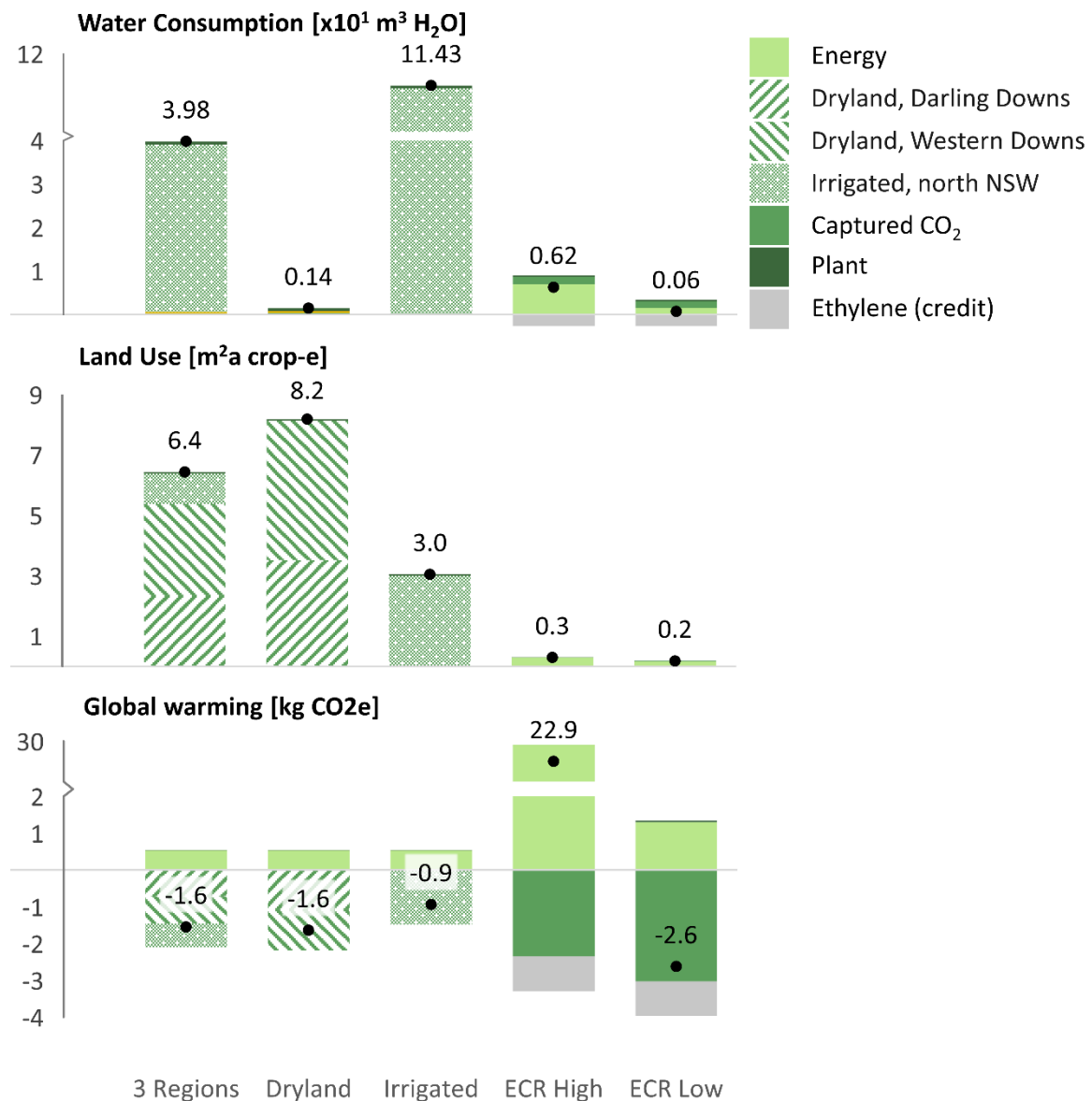


Fig. 5.8 Sensitivity analysis for water consumption, land use, and global warming using different sorghum sources

While the water use of dryland sorghum bioethanol becomes competitive with the best-case scenario of the ECCR, the land use increases by 27% from the 3-Regions case, requiring up to 29-50 times the land necessary for the ECCR system. In comparison,

the ECCR requires only 2-3% and 3-4% of the land necessary for Dryland and 3-Regions bioethanol, respectively. Using only Dryland sorghum has a marginal improvement (-6%) on GWP. When using only irrigated sorghum, the land use is more than halved, but the GWP increases by 39% and the WC is increased almost three-fold.

For the effect of using renewable energy directly for the sorghum process in the other impact categories besides GWP and ADP, it should be evident that the improvement would only be marginal given the substantially higher impact associated with sorghum itself rather than the energy used. Figure 5.9 shows the potential impact in all impact categories for the ECCR and reference system for all electricity scenarios, including the reference using entirely electricity at the Low-CI scenario. Although rarely performed, conducting a sensitivity analysis on the benchmark is important to better understand the process and trust its integrity as the standard for comparison in the assessment (von der Assen et al. 2013).

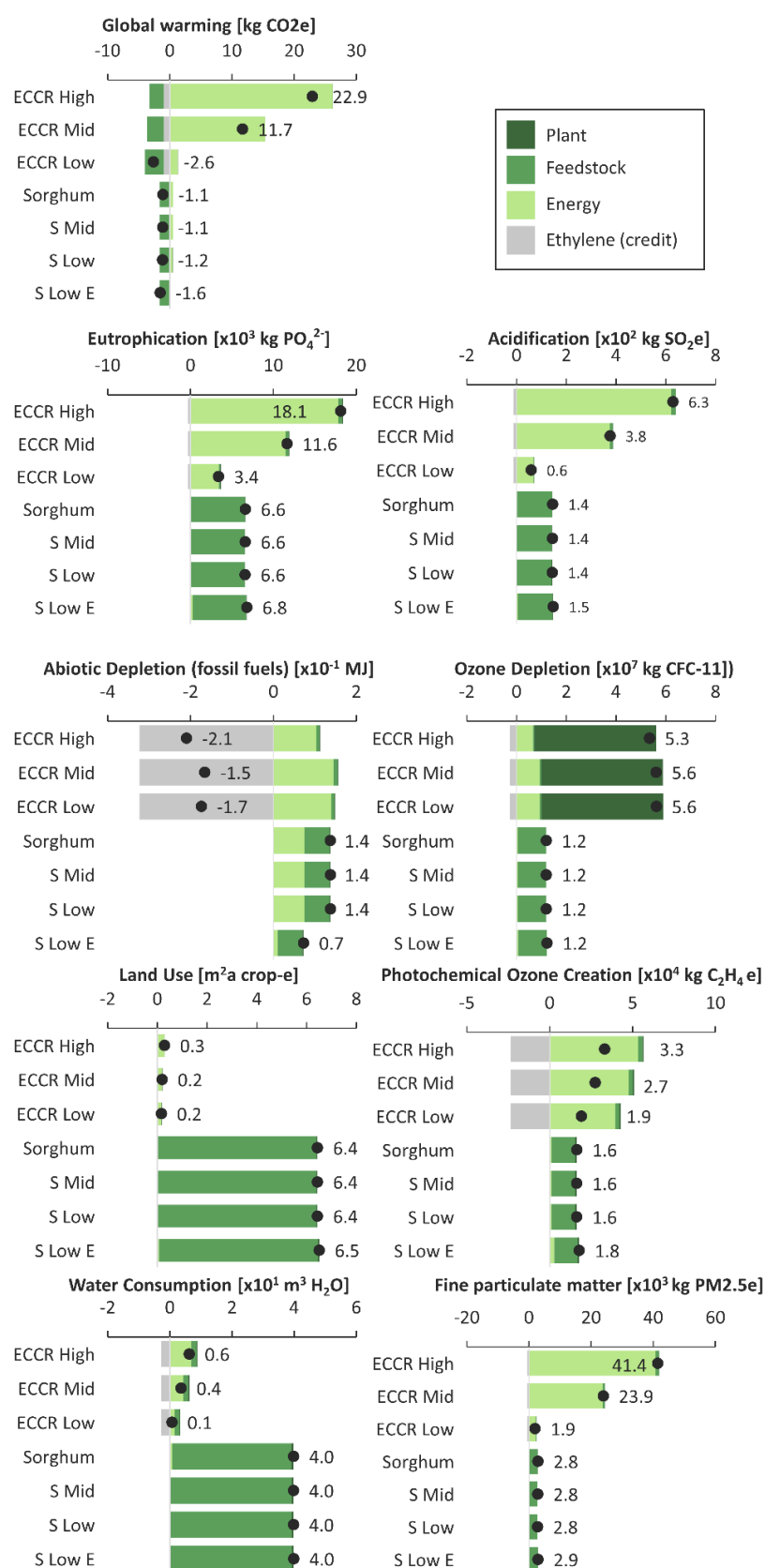


Fig. 5.9 Potential environmental impacts in all categories for the electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system and sorghum bioethanol (S) using electricity from the three different scenarios (High, Mid, Low) and the fully electric bioethanol process using Low-Cl electricity (S Low E)

### 5.2.5 Electrolyser sensitivity analysis

As the electrocatalytic process is an early-stage technology, a sensitivity analysis is helpful in identifying the environmental hotspots in the electrolyser itself. Figure 5.10 shows the relative contribution of the main subcomponents of the electrolyser. While the assembly has a high relative contribution to several impacts (mainly from the steel used in the casing), the only categories where the electrolyser has a contribution above 1% of the entire ethanol production are ODP, POCP, AP, and FPMF. The use of PTFE in the cathode and in the assembly constitutes most of the impact in ODP, while the use of nickel in the anode represents the highest contribution in the other three categories. Potential improvements could be achieved by using alternative materials for the electrodes. For the anode, using a different electrode with a lower overpotential for the oxygen evolution reaction (OER) would also reduce the energy requirements of the system (Haas et al. 2018) and its associated impacts to POCP, FPMF, and AP.

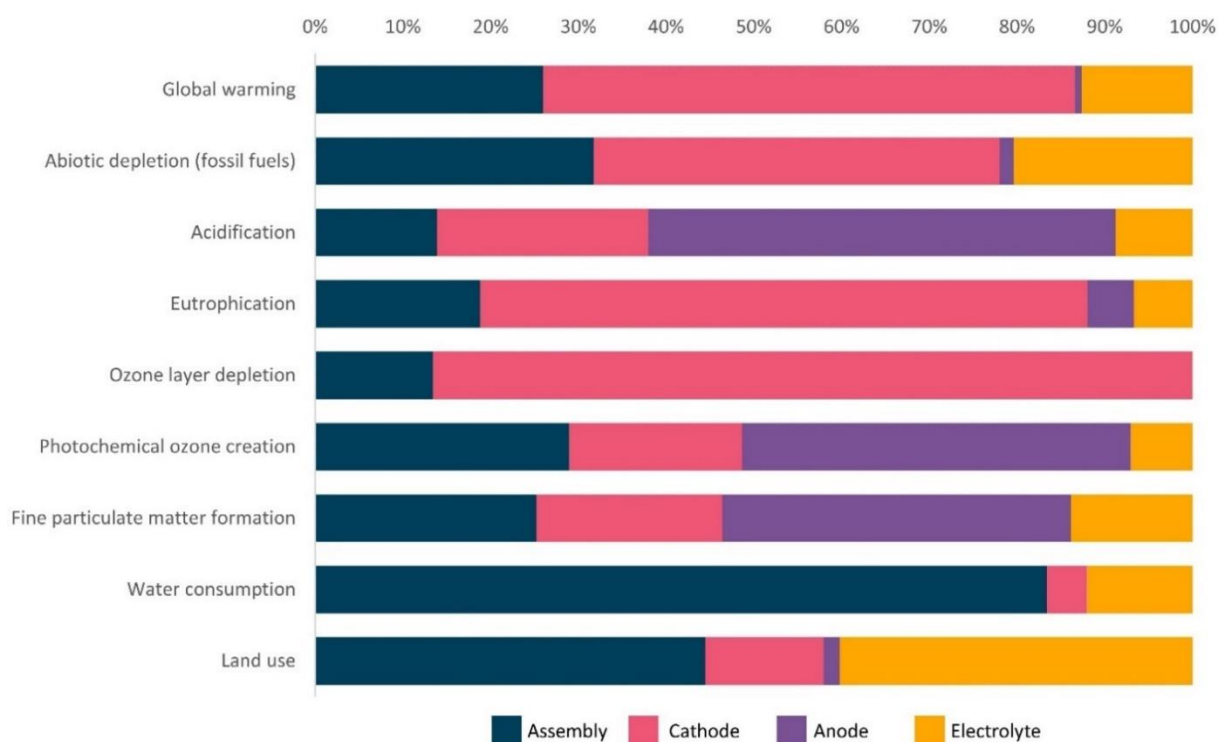


Fig. 5.10 Relative contribution of the subcomponents of the electrolyser (assembly, cathode, anode, and electrolyte) to the examined environmental impact categories

In the cathode preparation, a PTFE membrane is used to sputter the N-C/Cu catalyst. While a substitute material could be used, only reducing the thickness of this membrane could present substantial benefits. As described in its inventory in Section B1.2.2, the inventory assumes the average thickness of the specific commercial product used in Wang *et al.* (2020) to calculate its required mass. A sensitivity analysis on using a membrane thickness within a commercial range is shown in Figure 5.11. If the thickness of the PTFE spacers in the assembly is reduced to 0.5 mm, the PTFE membrane thickness of the layer in the cathode would need to be 28µm to match the ODP of the reference system. Future improvements in current density would also reduce the electrolyser footprint proportionally and the associated ODP from the use of PTFE.

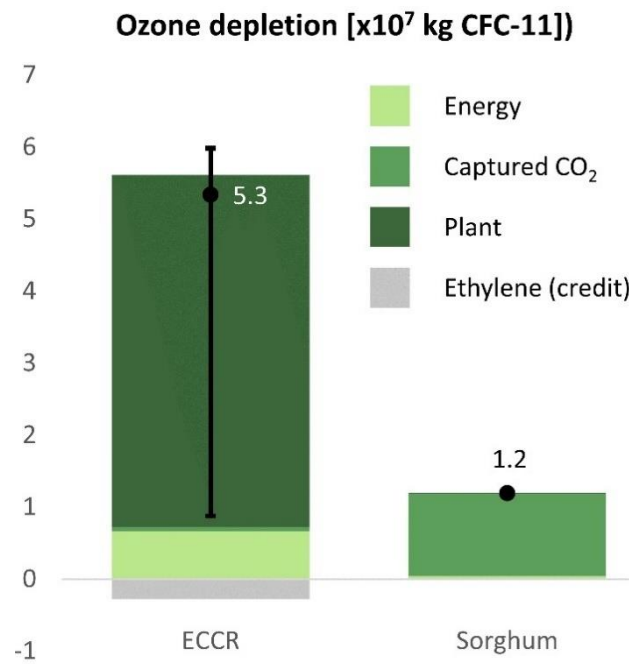


Fig. 5.11 Effect of the PTFE membrane of the cathode to the ozone depletion potential compared to the reference. The range of PTFE membrane thickness is 10 – 270  $\mu\text{m}$

To explore the effect of using a non Ni-based electrode in the anode, the electrolyser was re-modelled using a Fe-Co composite film on a carbon fibre paper (CFP) as the one synthesised and characterised by Liu *et al.* (2017). The authors reported a high OER performance in a 1M KOH electrolyte, with an overpotential as low as 283 mV. This anode also has an economic advantage of not requiring high purity nitrogen for its manufacture. More information on the inventory of this electrode can be found in section B1.7.

Figure 5.12 shows the relative difference between the impacts of the assembled electrolyser with Ni foam and Fe-Co composite film on CFP as anodes. Using the Fe-Co anode decreases the AP, POCP, and FPMF of the electrolyser in 52%, 42%, and 38%, respectively. While there is a marginal decrease in EP (3%) and increase in ADP (3%), the rest of the impact categories remain constant.

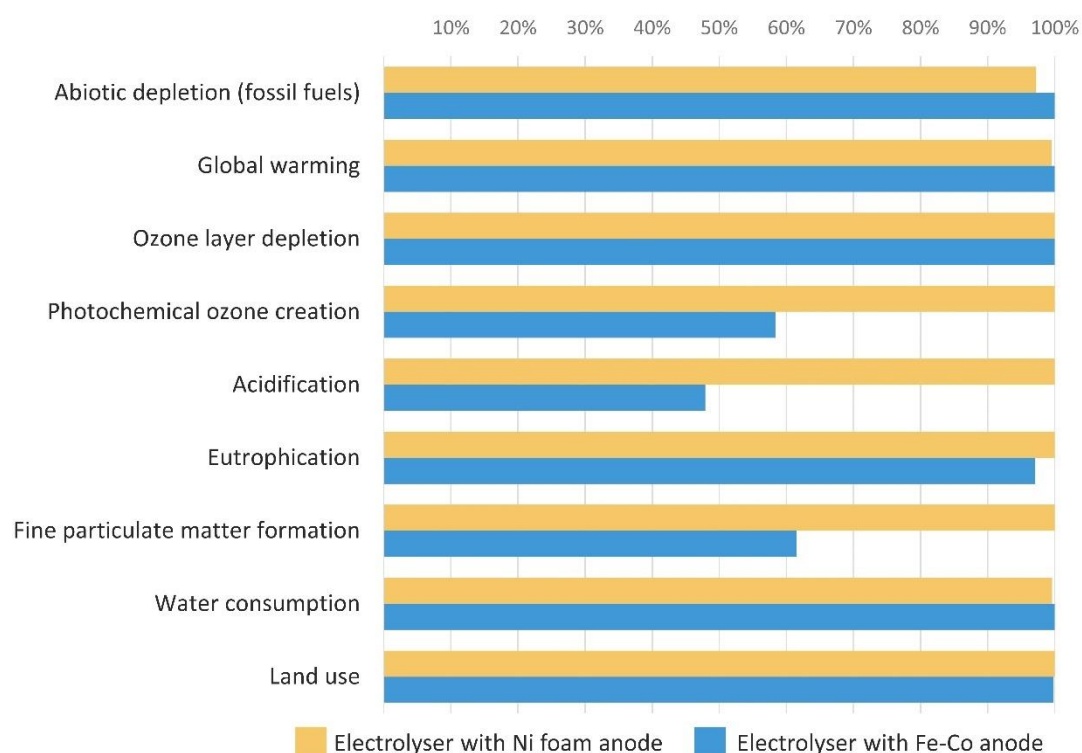


Fig. 5.12 Relative comparison in environmental impacts with the electrolyser using a Ni foam anode and a Fe-Co anode

The potential environmental impacts were re-calculated using this catalyst and an overpotential of 283 mV to offer a perspective on the sensitivity of the examined impacts to the total voltage applied. This reduced overpotential results in an energy reduction of approximately 5%, with a total power input of 203 MW for the electrolyser and a total energy requirement of 25.7 kWh/kg ethanol. While this anode reports a lower overpotential compared to the Ni foam anode, the Fe-Co anode would need to be tested in this particular system to confirm its improved performance.

Figure B1 shows the potential impacts in all categories for the ECCR system using the Ni foam anode, the sorghum bioethanol reference, and the ECCR using the Fe-Co anode. The differences are expectedly more marked in the High-CI scenario because of its share of fossil fuels in electricity generation. Table 5.4 shows the relative reduction in each impact category with a heatmap of the largest reductions. The largest reduction is found in POCP for the Low-CI scenario. Under these conditions, using this anode reduces its POCP to be comparable to the sorghum bioethanol reference.



Additionally, Figure B2 shows the CI sensitivity analysis, indicating that the breakeven with the reference sorghum is increased to 94 g CO<sub>2</sub>/kWh and with the all-electric to 83 g CO<sub>2</sub>/kWh.

Table 5.4 Percentage reduction in all examined environmental impact categories of ethanol production via ECCR in every carbon intensity (CI) electricity scenario when using the Fe-Co anode compared to using the Ni foam anode. Intensity of colour indicates a higher reduction

Impact assessment category	Percentage change vs ECCR with Ni foam anode in scenario		
	High-CI	Mid-CI	Low-CI
Global warming	-7.18%	-8.23%	-3.12%
Eutrophication	-6.19%	-6.22%	-6.46%
Acidification	-6.33%	-6.46%	-8.26%
Abiotic depletion (fossil fuels)	-3.06%	-5.50%	-5.03%
Ozone layer depletion	-0.78%	-1.04%	-1.05%
Land use	-6.22%	-6.26%	-6.20%
Photochemical ozone creation	-10.90%	-11.89%	-14.40%
Water consumption	-1.01%	-1.64%	-8.71%
Fine particulate matter	-6.23%	-6.30%	-8.30%

Finally, a sensitivity analysis was performed to gauge the effect of the lifetime of the cathode in all environmental impacts. The lifetime of the catalyst in this model was assumed to be 5,000 hours, as a conservative average stack lifetime of large-scale polymer electrolyte membrane fuel cells, which have a considerably shorter lifespan than alkaline systems (Myers et al. 2012). Figure 5.13 shows the effect in the examined environmental impacts varying this parameter from 500 hours (an order of magnitude lower than the assumption), 2,500 hours, 10,000 hours, and up to 60,000 hours, which is the lifetime of the rest of the components in the assembled electrolyser.

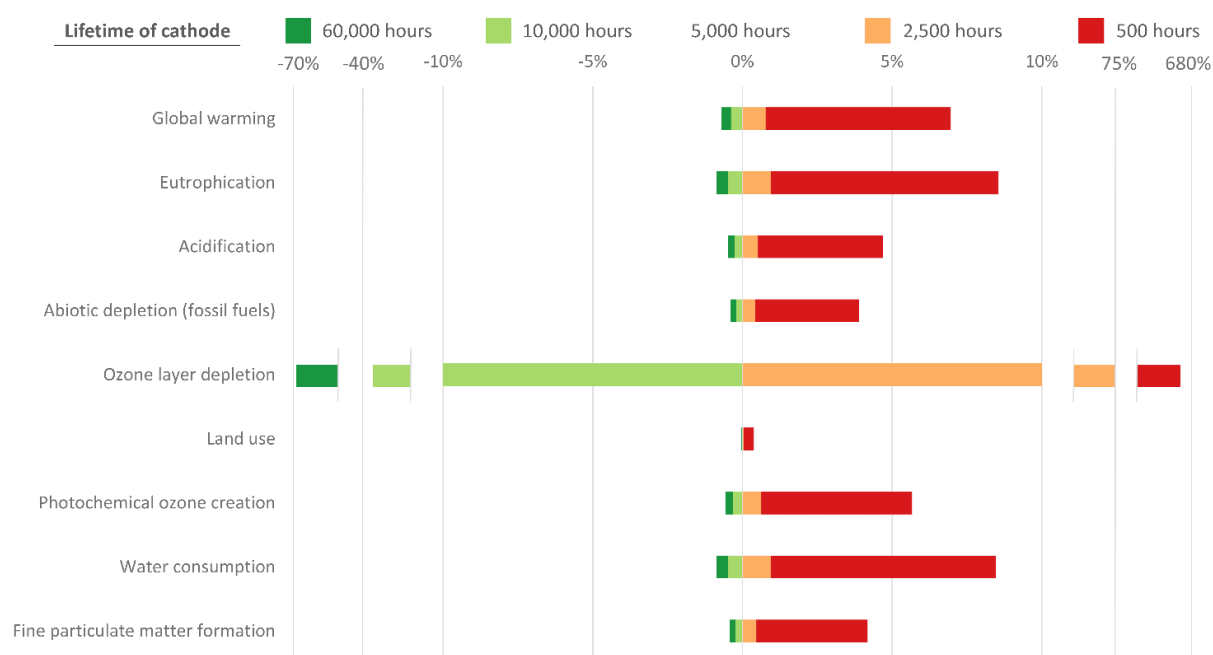


Fig. 5.13 Sensitivity analysis on the effect of the lifetime of the catalyst in the ECCR system using the Low-CI scenario for all examined environmental impact categories. The range of the lifetime is 60,000 hours, 10,000 hours, 5,000 hours, 2,500 hours, and 500 hours

The analysis indicates that, besides its effect on ODP, there is no significant difference in assuming a lifetime of 2,500 hours or 60,000 hours in the Low-Ci scenario. The difference in all impact categories between 2,500 and 60,000 hours is within only 2%. Even when the lifetime is reduced to 500 hours, there is an average increase of approximately 5% in all categories except ODP. The most sensitive category is the ODP, showing a decrease of up to 38% and 69% when increasing the lifetime to 10,000 and 60,000 hours, respectively. In contrast, the ODP increases in 75% and in 677% when the lifetime is reduced in half and in one order of magnitude, respectively.

Figure 5.14 then includes the impact of the ECCR using the High-CI scenario electricity and the sorghum bioethanol reference to show the relative comparison of total impacts with error bars accounting for the variability of the effect of the lifetime. The plot shows that the ECCR at the High-CI scenario offers a benefit in ADP, LU, and WC at any value of the examined range of cathode lifetimes. The ECCR at the Low-CI scenario demonstrates a benefit in the rest of the categories with the exception of ODP and POCP, which require the aforesaid changes of PTFE layer thickness

reduction and substitute use of an Fe-Co anode to make the impact comparable to the reference.

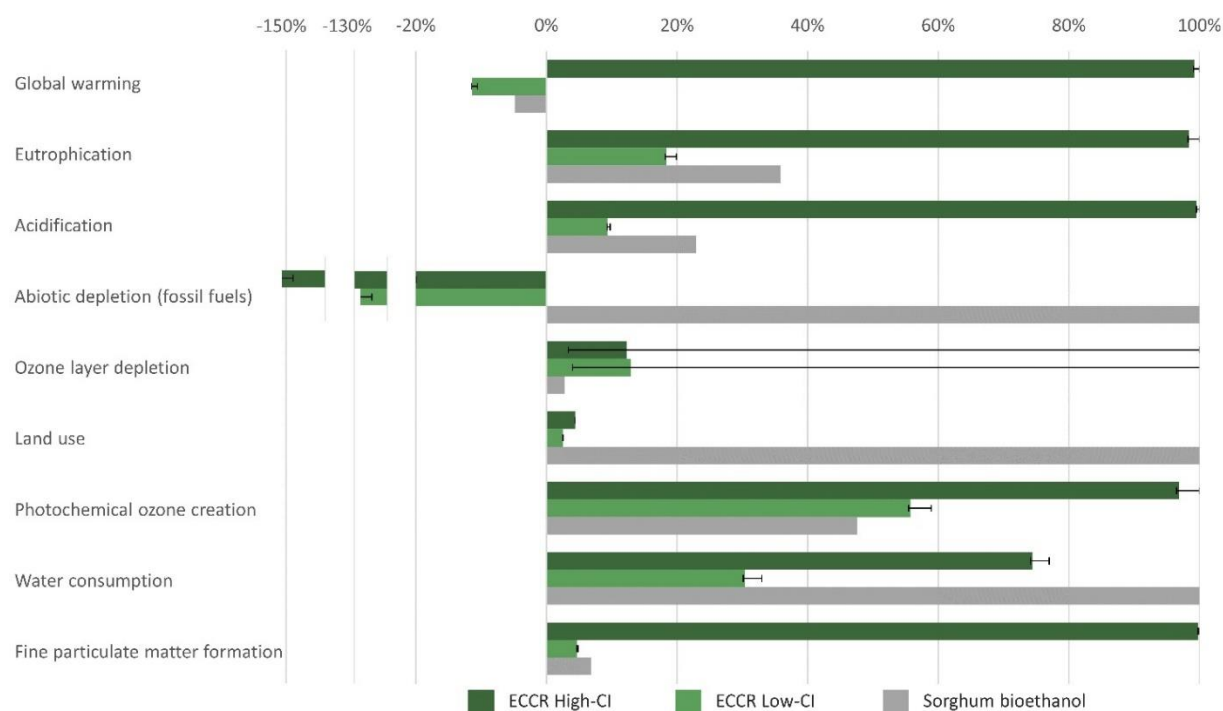


Fig. 5.14 Sensitivity analysis on the effect of the lifetime of the catalyst in the ECCR system cathode using High and Low carbon intensity (High-CI and Low-CI) electricity scenarios for all examined environmental impact categories. Bars show impact at a lifetime of 5,000 hours with error bars for a lifetime of 500 hours to 60,000 hours. With the exception of ozone layer depletion (ODP), the difference between the impact of 5,000- and 60,000-hours catalyst lifetime is marginal

From a carbon footprint perspective, the ECCR at the Low-CI scenario and a cathode lifetime of 500 hours is still more competitive than the reference. To determine the breakeven lifetime of the catalyst that matches the GWP with that of the sorghum bioethanol reference, Figure 5.15A plots the GWP of ethanol production by varying the lifetime between 10 – 500 hours. The y axis was transposed by 3 units to keep the values positive. The fitted curve appears to be a power function. However, when the logarithms of these points were plotted in Figure 5.16B, the analysis indicated the logarithms follow a 3<sup>rd</sup> order polynomial curve. As the values of GWP were transposed by 3 units, the carbon footprint of the reference to match is 1.88 kg CO<sub>2</sub>/kg ethanol. Thus, the lifetime of the cathode to breakeven with the sorghum bioethanol is only 66.5 hours from a carbon footprint perspective.

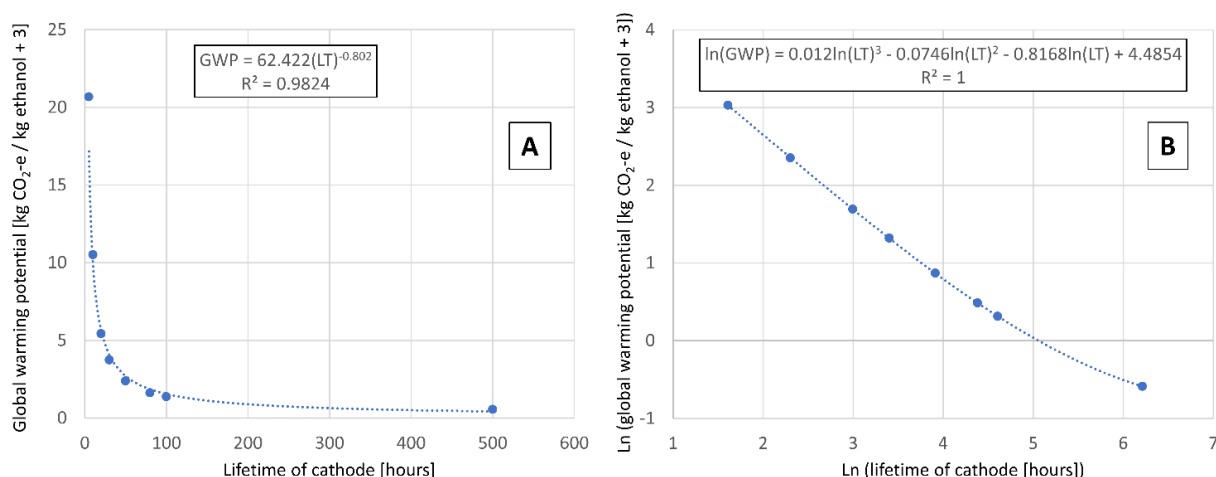


Fig. 5.15 Relationship between the lifetime of the cathode and the global warming potential of ethanol via the electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system

## 5.2.6 Discussion

This assessment maintains the analysis at Midpoint impact categories to reduce the uncertainty of the results. Given the low technology readiness level (TRL) of the process and the associated uncertainty in the data, extending the assessment to Endpoint categories would reduce the reliability of the comparison. Moreover, normalisation was not performed because the quality of normalisation data for Australia does not cover the entire range of chemicals involved, potentially providing misleading results (Grant et al. 2014). Nevertheless, the purpose of this assessment is to provide a direct comparison of the proposed CCU pathway against the reference process.

The carbon footprint of ethanol via ECCR requires electricity with a CI lower than 80 gCO<sub>2</sub>e/kWh to be more competitive than the reference. While the current CI of Queensland and the average CI of Australia overall are high (711 gCO<sub>2</sub>e/kWh), in Tasmania with 35 gCO<sub>2</sub>e/kWh (Australian Energy Market Operator 2020b), this process would already have a substantial advantage compared to sorghum bioethanol. These results also indicate that, depending on the variability of particular conditions, other regions around the world may also benefit from this technology. For perspective,

France with 43 gCO<sub>2</sub>e/kWh (AIB 2020) or British Columbia in Canada with 19 gCO<sub>2</sub>e/kWh (Environment and Climate Change Canada 2021) could produce ethanol via ECCR without requiring an agriculture subsystem and its associated water consumption and land use.

Therefore, this system offers an opportunity for regions where growing crops is limited or where a source of renewable energy is readily available. Since the ECCR only needs captured CO<sub>2</sub> as feedstock, it can be positioned anywhere and scaled to the necessary magnitude. The cost of feedstock for bioethanol represents 78-84% of its gross cost (Geoscience Australia and BREE 2014), which could present problems if the price of crops fluctuates. Additionally, 1<sup>st</sup> and 2<sup>nd</sup> generation feedstock may be tied to a growing season and would require storage to be used all year round. Storage of certain feedstocks can be challenging or affect its fermentation quality (Pordesimo et al. 2005). Using only CO<sub>2</sub> as feedstock in the ECCR system has the potential to reduce the uncertainty in the production costs and logistics for ethanol. As Saunders *et al.* (2011) concluded, avoiding the need of agricultural land and associated impacts with cultivation may offer a long-term solution to sustainable bioenergy generation.

With the rise of RE generation in specialised zones throughout the country (Australian Energy Market Operator 2020a), this ECCR system could be positioned next to a renewable energy generation source and act as a renewable energy vector for surplus energy. Apart from its modularity, the ECCR has a fast response time, making it suitable for intermittent renewable sources (Jouny et al. 2018). The storage and distribution of this energy using existing infrastructure for carbon-based fuels offers a benefit in isolated areas in Queensland and Australia overall. This has the potential to connect decentralised supply and demand points, increasing the flexibility of the energy system in the country and the security of the fuel supply chain (Abdin et al. 2019).

As mentioned in the methodology, DAC was used in the assessment to provide a fair comparison against the reference system with both processes capturing CO<sub>2</sub>

directly from the atmosphere. The use of DAC for captured CO<sub>2</sub> allows the system to be located in isolated areas with available renewable resources and inefficient transmission networks (Liu et al. 2020). Nonetheless, the CO<sub>2</sub> used could be obtained from a source with a higher initial concentration, requiring less energy to supply it to the electrolyser at the necessary conditions. Besides flue gasses from fossil fuel power generation, waste emissions from manufacturing processes such as ammonia production from natural gas or cement production can be a source of high purity CO<sub>2</sub> at low cost (García-Gusano et al. 2015). Even the emissions of the fermentation in bioethanol production could be the source of CO<sub>2</sub> (Müller et al. 2020), opening the opportunity for an integration between the two studied processes in this assessment for an increased ethanol production.

The electrolyser and proposed product separation system were scaled to meet a commercially-relevant output. While this modular scaled-out design provides flexibility to fit to any desired magnitude in market demand (Brennan 2002), it may become restrictive from an economic and engineering consistency perspective (Gavriilidis et al. 2002). Future developments on the design of the electrolyser or electrodes could increase the current density of the cathode. This would reduce the size and material requirements and decrease the energy requirements for the CO<sub>2</sub> conversion, having a significant reduction in the overall impact of the ethanol production. In the practical scaling of the electrolyser, different improvements will need to be developed to ensure catalyst stability since it is the biggest challenge in scaling up to an industrial-scale (Qiao et al. 2014).

Additional data on the stable efficiency of the electrolyser at extended periods of operation is required. If the performance of the same continuous electrolyte is maintained at a longer period, the concentration of ethanol in the stream towards the distillation unit would be higher and the associated separation energy requirements lower. It is also important to demonstrate the lifetime of the catalyst at a commercial

scale. While the sensitivity analysis identified only mild environmental effects of a reduced lifetime, the ECCR system is unlikely to be economically viable with a catalyst lifetime below the order of thousands of hours (Dominguez-Ramos et al. 2015). Finally, the proposed substitute anode may be useful in decreasing environmental impacts and energy requirements, but requires testing in this system to confirm its efficiency at a higher current density. Therefore, considerable experimentation is still needed to test the limits of the performance of the electrolyser.

### 5.3 Interpretation and conclusions

The LCA confirms that ethanol production by the electrocatalytic reduction of captured CO<sub>2</sub> has the potential to be a sustainable pathway for CCU compared to the traditional process of sorghum fermentation. At the current configuration, three of the impact categories examined have a reduced impact compared to the reference: abiotic depletion of fossil fuels, land use, and water consumption. A reduced impact in global warming, eutrophication, acidification, and fine particulate matter formation is conditional on the renewable share of the energy supplied. The ECCR system achieves a comparable impact to the reference in photochemical ozone creation when a substitute Fe-Co anode is used, and in ozone layer depletion when the thickness of the PTFE layer used in the cathode is decreased. The carbon footprint of ethanol production through ECCR becomes competitive when the energy supplied to the system has a carbon intensity of 80g CO<sub>2e</sub> per kWh or lower.

The system is a promising non-food-based, versatile, and modular process that presents a clear advantage on land use and water consumption. Using CO<sub>2</sub> as feedstock, the ECCR can be located where agricultural resources are limited, becoming a sustainable alternative to existing bio-based ethanol production. Given its modular configuration, it can be scaled to any necessary magnitude. Additionally, when

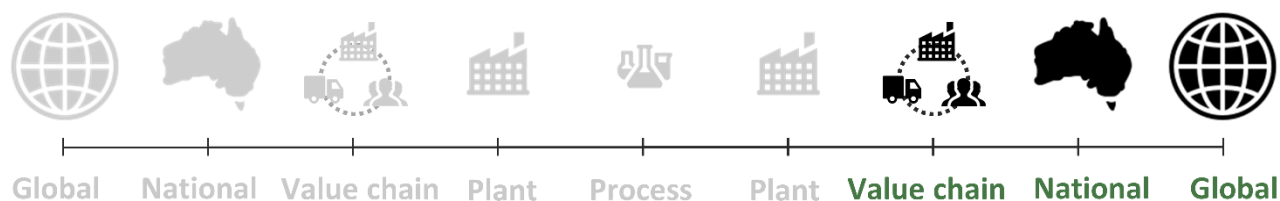
positioned in remote areas where renewable energy sources are available, it can be used as an energy vector for surplus energy, leveraging existing infrastructure for storage and distribution of carbon-based fuels.

Future research and scale-up testing is required to validate the potential benefits identified. Ethanol production through the electrocatalytic reduction of captured CO<sub>2</sub> has a low TRL and has not been analysed outside laboratory scale. Any future developments that increase the current density will have significant benefits in reducing the impacts associated with the manufacture of the stack. However, this type of assessment is useful to perform a screening analysis that estimate pertinent impacts and identify potential areas of improvement at an early stage (Zimmerman et al. 2018). This analysis was able to quantify the impact of the energy used in the system and prospective modifications to reduce environmental impacts, such as the use of a substitute for the nickel-based anode or a reduction in the use of PTFE in the cathode. Moreover, it confirms that the ECCR system has the potential to produce ethanol sustainably at a reduced impact in different environmental categories whilst offering the associated benefits of a CCU technology.

The LCA presented in the case study is not only compelling for its specific results, but also for being an illustrative case of a technology at early-stage which is screened to understand its environmental potential and prospective areas of improvement. As the industry practice is bio-based and not fully fossil-fuel dominant, the comparative LCA proves to be of excellent help in demonstrating potential benefits that are not evident from an environmental perspective. Additionally, technical improvements were identified regarding the materials used in the electrolyser and in the auxiliary systems for product separation, which may become crucial in the future scaling of this technology.



## 6 Discussion of the systematic approach



After the range of rigorous tools and mathematical models used in the framework, the discussion is brought back to a higher level to provide a discussion on pertinent aspects of the approach. Chapter 2 concluded stating the aim of this thesis: developing a single framework that links different models to help in the choice of a sustainable CCU technology for a specific region and quantify its potential environmental benefits. To determine if the proposed framework fulfils this purpose, the main components of sustainability should be re-examined.

For a process or system to be sustainable ultimately means that it meets the needs of the present without compromising the ability of future generations to meet their own (World Commission on Environment and Development 1987). It generally focuses on the characteristics of the overlapping economic, environmental, and social considerations of a studied system. These considerations have been included throughout the stages of this framework. Initially, the use of input-output analysis and modelling incorporates environmental and social layers to an economic evaluation. The selection of the specific chemical and region of study derived from economic potential and socio-political incentives. The life cycle assessment (LCA) examined in detail the specific

environmental burdens associated with an innovative system using a technology with low technology readiness level (TRL).

This chapter readdresses the economic, environmental, and social considerations of the proposed framework. It also provides an additional analysis on uncertainty and technological aspects to ensure the methodology and conclusions of the case study are robust. A final discussion emphasises the contribution of the framework and the case study and suggests complementary modelling approaches for prospective analysis.

## 6.1 Preliminary economic evaluation

Having identified a substantial potential for this technology from an environmental perspective, it will be fundamental to understand its economic viability. As the technology is at an early stage with a low TRL, a comprehensive economic assessment would have considerable inherent uncertainties. There can be substantial over- and underestimations in costs, as many components have never been manufactured at the scale modelled (Keith et al. 2018). Instead, a preliminary economic evaluation is able to gauge the magnitude of the investment required and identify if it is within a reasonable range.

This preliminary economic evaluation can be performed by estimating the operational costs from the inputs and outputs of the system and calculating a maximum value for the capital investment that allows an economic breakeven. The price of materials and chemicals in the final inventory can help estimate a simplified value for the total cost of the products and the cost of operating expenditure (OPEX) per functional unit. The subtraction of these quantities indicates the maximum value per functional unit associated with capital expenditure (CAPEX). The total CAPEX can be obtained through the equation for the levelized cost of the product (LCOP),

$$LCOP = \frac{CRF \cdot CAPEX + OPEX}{DC \cdot CF} \quad (6.1)$$

where CRF is the capital recovery factor (annualised), DC is the design capacity of the plant, and CF is the capacity factor. The capacity factor takes into account the plant availability.

For the evaluation of the ECCR system in the case study, Table 6.1 shows the prices and sources for each input and output of the system. Prices were adjusted for inflation and converted to 2021 US dollars (USD) using the historical currency exchange rates by Currency Converter (2021). The price of ethanol is the current spot price at Trading Economics (2021), which is similar to the levelized cost of sorghum bioethanol calculated by Peters and Ward (2016) in 2021USD: 0.498 USD/kg ethanol. The average price of ethylene used is \$1,010 USD/tonne according to the 5-year average in the Asian market price (IEA 2020a), which is consistent with the reference used in the recent ethylene techno-economic assessment by Sisler *et al.* (2021). The cost of captured CO<sub>2</sub> is based on the levelized cost from the original direct air capture (DAC) report (Keith et al. 2018), according to the configuration *D* of the system and a 7.5% CRF. O&M costs and capital were kept identical. Gas costs were removed and the electricity requirements were increased according to the inventory in the LCA. The electricity cost was calculated using the electricity wholesale price average for Queensland in 2021 shown in Table 6.1.

Table 6.1 Prices and operational costs of inputs and outputs of ECCR system

Outputs	Flow		Price		Source	Total (USD)
Ethanol	1	kg	\$0.486	USD/kg	Spot price, (Trading Economics 2021)	0.4862
Ethylene	0.416	kg	\$1.010	USD/kg	5-year average of Asian market price, (IEA 2020a)	0.4197
<b>Inputs</b>	<i>Total</i>					<i>0.9059</i>
Captured CO <sub>2</sub>	3.123	kg	\$0.090	USD/kg	Levelized cost of captured CO <sub>2</sub> , (Keith et al. 2018)	0.2801
Softened water	2.028	kg	\$0.002	USD/kg	Bulk water for business, (Queensland Government 2021)	0.0044
Cooling water	0.0009	m <sup>3</sup>	\$0.061	USD/m <sup>3</sup>	Surface water trade in Queensland, (Waterfind 2019)	0.0001
Electricity	30.168	kWh	\$0.032	USD/kWh	2021 price average in Queensland, (AEMO 2021)	0.9512
Water to wastewater	0.0002	m <sup>3</sup>	\$13.35	USD/m <sup>3</sup>	Non-residential sewerage volume charge * Load factor of 3, (City of Gold Coast 2021)	0.0023
<i>Operating costs</i>						<i>1.2380</i>

For the ECCR system, the DC and CF of Equation 6.1 are inherently considered in the production rate and lifetime specified for the system, producing 63.2 Mt ethanol/a (based on 8,000 operating hours per year). Assuming the LCOP to be equal to the revenue of the products and using the same CRF of 7.5% as the DAC plant (Keith et al. 2018), leads to a negative CAPEX, indicating the system is not economically viable based on the assumed economic parameters.

A sensitivity analysis on the price of electricity was developed to identify the conditions in which the ECCR system is viable. Since the main function of the system is to create products through electrolysis, the CAPEX can be normalised by the power rate of the electrolyser to encourage a more comparative metric for investment. Figure 6.1 shows the upper limit of the CAPEX normalised by the input power requirement of the electrolyser when varying the price of electricity. This power rate includes only the power input for the electrolyser without considering the auxiliary systems. The price of electricity would need to be lower than 20 USD/MWh to be economically

viable, as shown by the green shaded area under the curve. It is important to note that this breakeven is against market price of the products, which includes profit, tax, and other associated aspects additional to the cost of production.

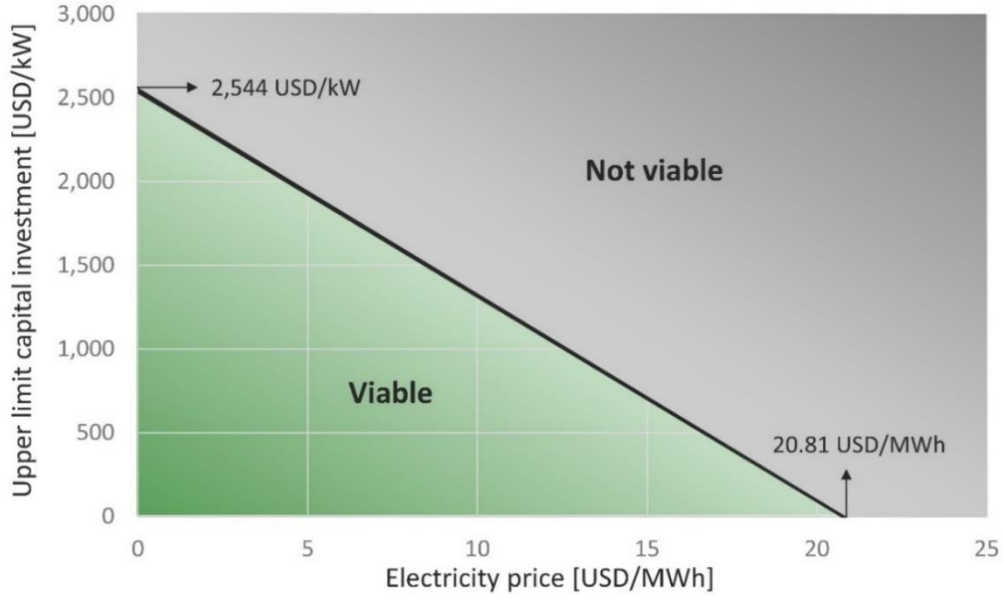


Fig. 6.1 Upper limit capital investment for return on investment according to the price of electricity

The cost of equipment ( $C_p$ ) can be estimated through the approach of Khalilpour and Zafaranloo (2020) in using the methodology of Turton *et al.* (2008) as follows,

$$C_{BM} = (B_1 + B_2)C_p \quad (6.2)$$

$$C_{TM} = (1 + \alpha_1 + \alpha_2) \sum C_{BM} \quad (6.3)$$

$$C_{FCI} = C_{TM} + \alpha_3 \sum C_{BM} \quad (6.4)$$

$$C_{TCI} = C_{FCI} + \alpha_4 C_{TM} \quad (6.5)$$

where,

- $C_{BM}$  is the cost of the bare module including direct and indirect costs regarding the installation of the purchased equipment that are quantified through the  $B_1$  and  $B_2$  constants;
- $C_{TM}$  is the total module cost including contingency ( $\alpha_1 \sum C_{BM}$ ) and contractor fees ( $\alpha_2 \sum C_{BM}$ );

- $C_{FCI}$  is the fixed capital investment cost that include site development, auxiliary buildings, off-sites, and utilities ( $\alpha_1 \Sigma C_{BM}$ );
- $C_{TCI}$  are the total capital costs or CAPEX that include working capital ( $\alpha_4 \Sigma C_{TM}$ ); and
- $B_i$  and  $\alpha_i$  are corresponding constants as fractions to each parameter cost.

Expressing the total capital costs in terms of the cost of equipment and the associated coefficients,

$$C_{TCI} = [(1 + \alpha_1 + \alpha_2)(1 + \alpha_4) + \alpha_3][(B_1 + B_2)]C_p \quad (6.6)$$

Using the middle points of the ranges in Turton *et al.* (2008) as estimates, the following constants can be assumed:  $(B_1 + B_2) = 1.5$ ,  $(\alpha_1 + \alpha_2) = 0.18$ ,  $\alpha_3 = 0.3$ ,  $\alpha_4 = 0.15$ . Then, the total capital costs can be expressed as,

$$C_{TCI} = 2.4855C_p \quad (6.7)$$

Thus, the estimated upper limit cost of equipment of the ECCR system, comprising the electrolysis stacks, adsorption, and distillation units, can be estimated from the total CAPEX. Figure 6.2 illustrates the sensitivity of the total cost of equipment to the price of electricity. According to the projections of CSIRO (Graham et al. 2020), the projected CO<sub>2</sub> prices range from approximately 20 USD/tCO<sub>2</sub>e in 2020 up to 200 USD/tCO<sub>2</sub>e in 2050 according to different temperature-limiting and technology-adoption scenarios. Thus, Figure 6.2 includes ranges for carbon credit that may be incorporated to identify the increase in the upper limit of the cost of equipment. This credit was added as income based on the amount of CO<sub>2</sub> captured and used in the inventory. As DAC is currently the most expensive method of sourcing CO<sub>2</sub> (IEA 2020d), a carbon credit is essential and justified to offset the increased costs.

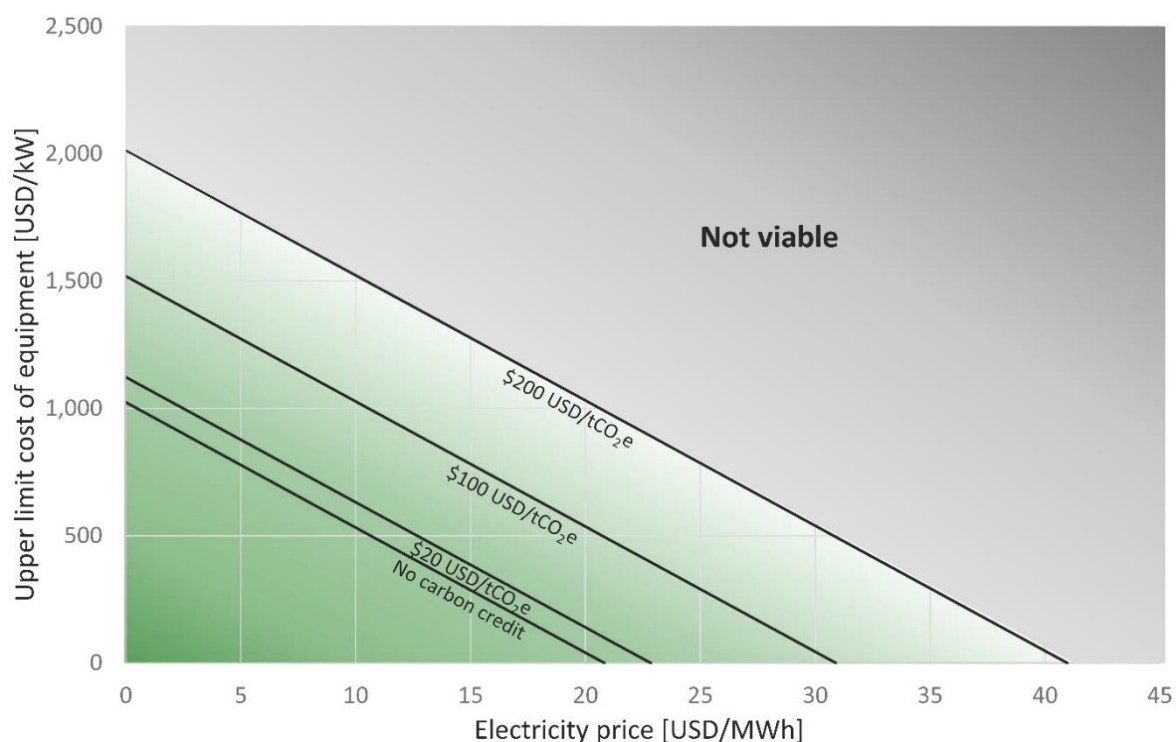


Fig. 6.2 Upper limit cost of equipment of the entire electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system at manufacturer's site according to the price of electricity with different levels of carbon credit

To offer a perspective on the historical cost of electrolyzers, Figure 6.3 illustrates the decrease of cost of alkaline electrolyzers per kW capacity from 2004 to 2020. Prices were adjusted for inflation and converted to 2021 US dollars (USD). The threshold for the upper limit cost of equipment of the ECCR system is included for every carbon credit scenario. It is important to reiterate that this cost of equipment includes the cost of equipment for the adsorption and distillation units besides the cost of the electrolyser itself. As the distillation and adsorption units scale at a power (typically around 0.6) but the electrolyser scales linearly beyond the capacity of the individual cell stack (Genovese et al. 2009), it is difficult to discern between the costs of each component. However, with the decreasing trend of costs and the further projected reductions by 2050 down to less than \$100 USD/kW for alkaline electrolyser stacks (IRENA 2020), the economics of the ECCR system appear to be within a feasible range to be economically viable and competitive with current bioethanol production.

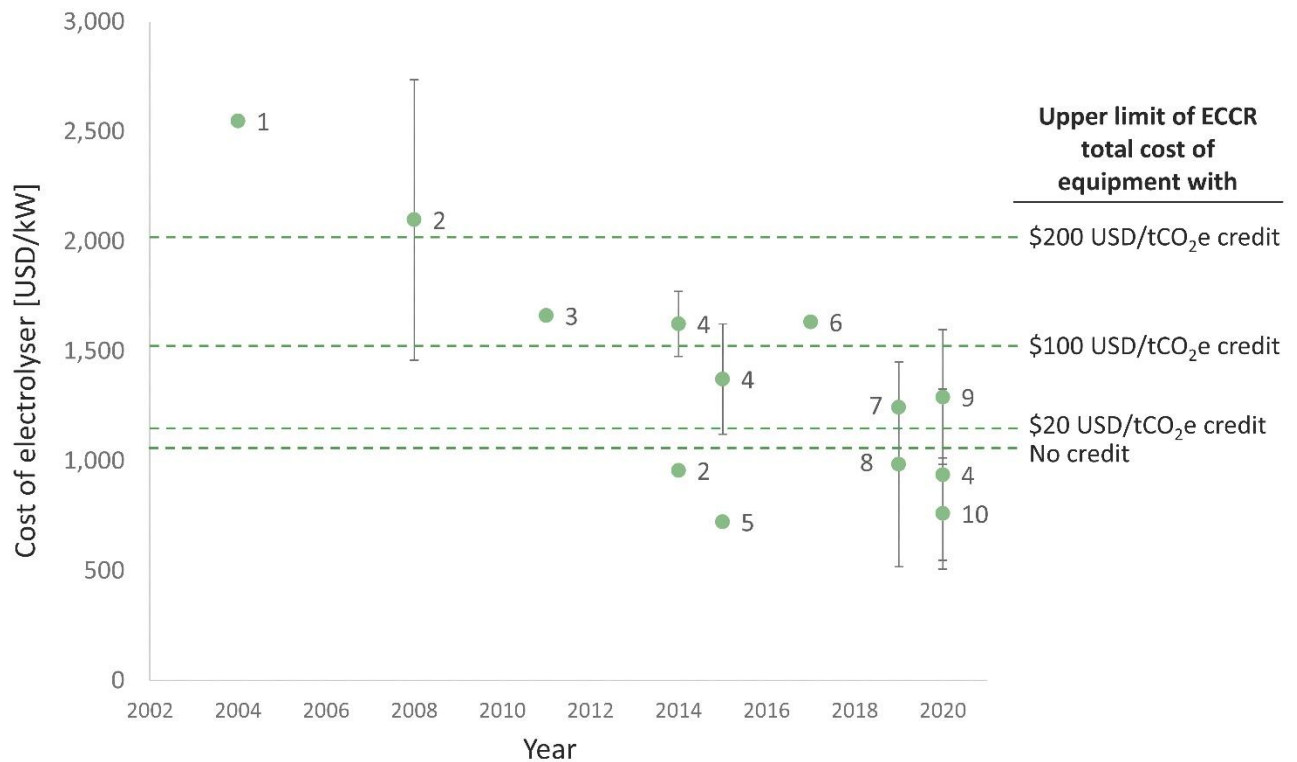


Fig. 6.3 Historical costs of alkaline electrolyzers and the threshold value of breakeven for the cost of equipment of the ECCR system. Numbers indicate the references for each point, detailed in Table 6.2

Table 6.2 References for points and ranges in Figure 6.3

Number in Figure 6.3	Reference
1	Zoulias <i>et al.</i> (2004)
2	Saba <i>et al.</i> (2018)
3	Smolinka <i>et al.</i> (2011)
4	Bertuccioli <i>et al.</i> (2014)
5	Gutiérrez-Martín <i>et al.</i> (2015)
6	Noack <i>et al.</i> (2015)
7	BloombergNEF (2019)
8	IEA (2019)
9	Schmidt <i>et al.</i> (2017)
10	IRENA (2020)

While this is a very preliminary calculation, it provides a notional magnitude for the economic costs necessary to make this system viable in the future. As the technology matures and pilot plant or commercial data become available, more detailed techno-economic assessments will be critical to provide a comprehensive understanding of the key economic parameters. The preliminary economic evaluation in this framework is



helpful for manufacturers in identifying opportunities to reduce capital cost or for policy-makers in promoting mechanisms that facilitate the viable construction and operation of such systems.

## 6.2 Environmental considerations

The environmental guidelines and considerations have been exhaustively covered, quantifying the potential environmental impacts of the proposed system. Sensitivity analyses were also useful in determining pertinent thresholds or scenarios in which the system presents a benefit compared to the reference. The purpose of performing these analyses within an LCA is to provide rigorous insights that help in taking an informed decision. In the context of the present framework, these decisions revolve around the *if* and *how* to implement a specific CCU technology. Therefore, the validity of the insights needs to be carefully examined. Uncovering the uncertainties associated with the assessment is fundamental to this purpose.

### 6.2.1 Parameter uncertainty

Chapter 5 introduced a categorisation of types of uncertainty according to parameters, model, and choices. The same chapter already included a comprehensive sensitivity analysis on key parameters, such as the thickness of the PTFE layer in the cathode. Parameter uncertainty is related to data quality and it may be solved by improving the accuracy of the data through iteration and continuous narrowing of the realistic range of key variables on inventory compilation (Huijbregts et al. 2003).

This is important as well for emerging technologies, where the disposal or recycling processes of particular subcomponents are not defined. General assumptions on the fate of materials will be substituted for more realistic processes. Production process data from proprietary chemicals, such as the ones in the elaboration of the

electrolyser, can become a challenge to model correctly. Software tools are normally required to estimate the energy and environmental stressors according to general molecular characteristics (Wernet et al. 2009). However, relying entirely on current databases or estimations will only offer a partial assessment of the chemicals used around the world. Collaboration with the associated companies is normally one of the best ways to model correctly such processes.

### 6.2.2 Model uncertainty

It is also important to understand the uncertainty in models associated with the assessment and how they accurately represent a real system. An example of model uncertainty is that associated with the fate of the emissions beyond the primary impact or damage category. Siirila *et al.* (2012) discussed an illustrative situation, where CO<sub>2</sub> emissions can play a role in potable water systems, decreasing pH and allowing toxins that can influence human health impacts. The fate of the entire range of chemicals should be modelled in the same rigorous way as the radiative forcing of CO<sub>2</sub> discussed in Chapter 3. Notwithstanding its difficulty, modelling such low probability but high impact events should be considered in comprehensive assessments (Sathre et al. 2012). This also applies to modelling uncertainty in the simulation of processes compared to a real pilot-scale or commercial plant operational data.

A significant model uncertainty related to the core methodology presented in this framework is the one associated with the characterisation factors in the impact assessment method of the LCA. As it was of much focus in Chapter 3, the characterisation values for GWP in the input-output model were based on a 20-year horizon rather than the common practice of 100-year horizon. The purpose of this selection was two-fold: the results are in a shorter time span that is more in line with the timeframe of required climate action, and the uncertainty associated with the metric itself is reduced.

The LCA thus far has used the 100-year horizon for GWP, which is the common practice for the CML impact assessment methodology. This is also the recommendation in LCA guidelines (IEAGHG 2018; Skone et al. 2019; Zimmermann et al. 2020). Figure 6.4 shows the difference between the ECCR system at the High, Mid, and Low carbon intensity scenarios and the sorghum reference when using a 100-year and 20-year horizon. Using the 20-year horizon characterisation values increases the impact by 9% for the High-CI scenario, by 10% for the Mid-CI scenario, by 2% for the Low-CI scenario, and 5% for the sorghum reference. There is an increase in impact of 8-9% according to energy, 0.2-2.5% in feedstock and 53% according to plant. The ethylene credit has an associated increase of 9%. The plant component has such a pronounced relative increase because of the disposal of plastics at the end of life of the electrolyser and its use of PTFE in the cathode and as a spacer in the electrolyser assembly. Methane from landfill/incineration and chlorofluorocarbons in the manufacture of PTFE contribute to this difference as these emissions have considerably higher GWP characterisation values in a 20-year horizon (see Table 3.1).

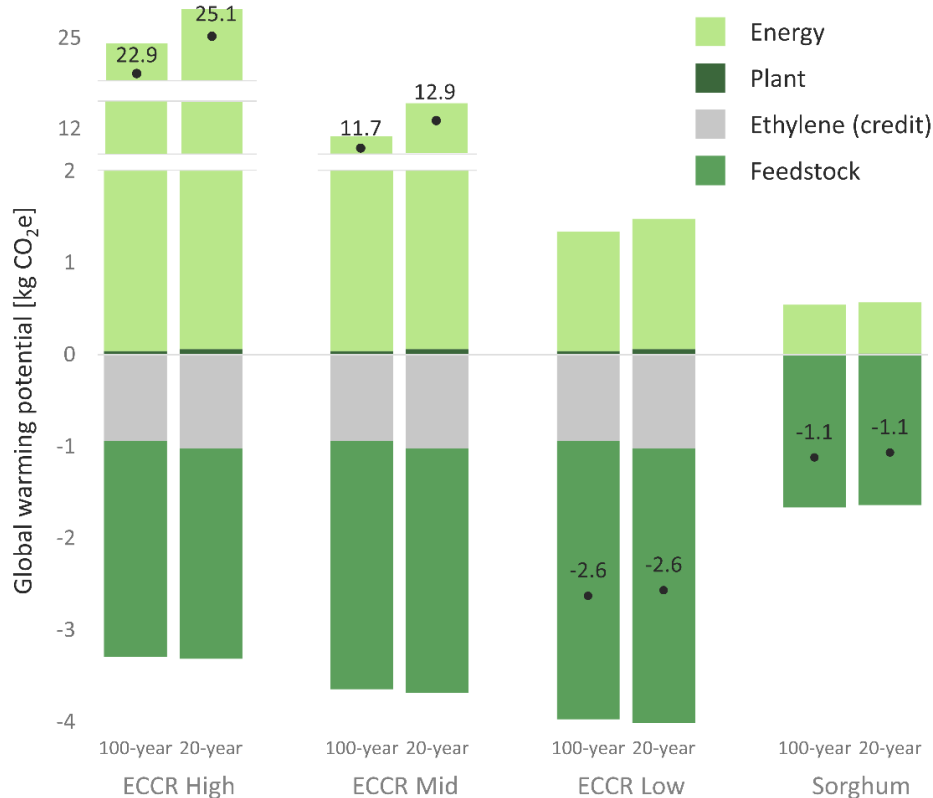


Fig. 6.4 Difference in the global warming potential of the ECCR system at the different carbon intensity scenarios and the sorghum reference with characterisation values for a 100 and 20-year horizons

At a lower carbon intensity grid, the difference in the results between the two horizons is reduced. Figure 6.5 shows the sensitivity analysis of the carbon footprint of both systems using the 20-year horizon. The breakeven between the ECCR system and bioethanol sorghum reference is found when the energy used has a carbon intensity of 84 g CO<sub>2</sub>/kWh, a difference of less than 6% compared to using 100-year horizon factors. Therefore, the difference of horizons in this case is marginal. However, it is important to check this and confirm the characterisation values used are consistent. While guidelines encourage the use of 100-year horizon GWP values to improve harmonisation and comparability between assessments, the 20-year horizon is also helpful in identifying the potential effect at a shorter lifespan. This is especially useful in current times with environmental targets for 2030 and 2050.

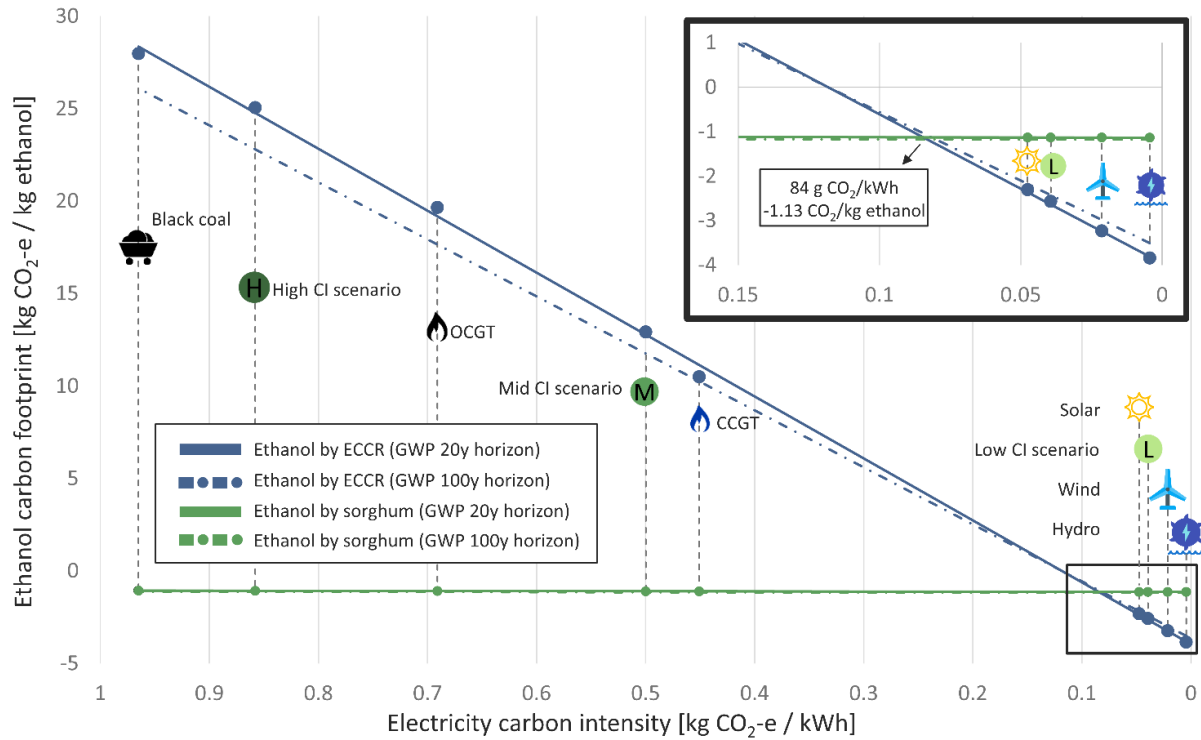


Fig. 6.5 Carbon footprint of ethanol production by ECCR (blue line) and by the sorghum reference (green line) using a global warming potential characterisation factor based on a 20-year horizon (continuous line) and a 100-year horizon (dash-dotted line) with electricity of different sources and carbon intensity.

*Icons taken from open-source websites*

*icons8.com and cleanpng.com*

### 6.2.3 Uncertainty due to choices

The uncertainty due to choices is linked to the particular decisions of the practitioner in the construction of the LCA, such as the cut-off of the system boundaries or the method of solving multifunctionality. These choices can have a great influence in the message conveyed and the conclusions that can be drawn from it. The following two subsections will provide a different scenario of the multifunctionality solution and system boundaries selection in the case study and illustrate the effect of these choices.

#### 6.2.3.1 Multifunctionality solution

In the case study presented, the by-product of the sorghum bioethanol -dry distiller's grains with solubles (DDGS)- is solved by allocation. This decision was taken as the database was comprehensively created by multiple organisations with scrutiny.

However, it can also be solved through system expansion by substitution, using the same method for solving multifunctionality in both processes.

As mentioned in the previous chapter, DDGS is used as a high-protein feed for cattle. Therefore, the substitute needs to maintain a similar function. Two potential substitutes for such feed were selected: cottonseed meal and soybean meal. These are by-products themselves of crops grown in the area of study, high in fibre and protein similar to DDGS. Each of them is obtained through the main process of extracting oil from each respective crop. The equivalence to fulfil the same function of DDGS was based on protein content, as is the common practice for feed substitution (Jonasson & Sanden 2004). The amount of DDGS in the reference sorghum system is 0.892 kg DDGS/kg ethanol. The equivalent quantity for each substitute was proportionately calculated according to the quality of the substitute feed products shown in Table 6.3.

---

Table 6.3 Protein quality for sorghum dry distiller's grains with solubles (DDGS), cottonseed meal, and soybean meal

---

Feed product	Dry matter (DM) (%)	Protein content (% DM)	Reference
Sorghum DDGS	90	34	(Heuze et al. 2015)
Cottonseed meal	92	45	(Heuze et al. 2019)
Soybean meal	88	53	(Heuze et al. 2020)

---

The inventories of both substitutes were taken from LCI databases and adapted to account for atmospheric and biogenic CO<sub>2</sub> emissions and the electricity mix of the assessment. The inventory of soybean meal was taken from the ecoinvent 3.5 database (Wernet et al. 2016). The inventory of cottonseed meal was taken from the AusLCI database (Edge Environment & Lifecycles 2016), which was specifically compiled in detail by Grant *et al.* (2014) for the Rural Industries Research and Development Corporation of the Australian Government.

Figure 6.6 shows the relative change in each environmental impact category of producing ethanol via sorghum fermentation with the two substitute products

compared with the allocated reference. With the exception of photochemical ozone creation potential (POCP) and GWP, all impacts are increased as a result of a lower credit from the substitutes than from the allocated impact to DDGS. The global warming potential (GWP) is technically reduced because the negative value for the carbon mitigation associated with cottonseed or soybean meal is lower than the allocated one to DDGS. Hence, the offset of the cottonseed or soybean meal to the entire coproducing reference process results in a lower total GWP than when the allocation removes the carbon mitigation associated with DDGS. The variability in associated impacts is a consequence of different characteristics of each crop and the lower amount required from each substitute. The POCP of ethanol when using soybean meal as substitute is the only category where there is an actual impact reduction. This decrease of 52% compared to the allocated process is a result of increased  $C_2H_4$  emissions associated with hexane used in the solvent extraction process of soybean oil (Dunford 2012).

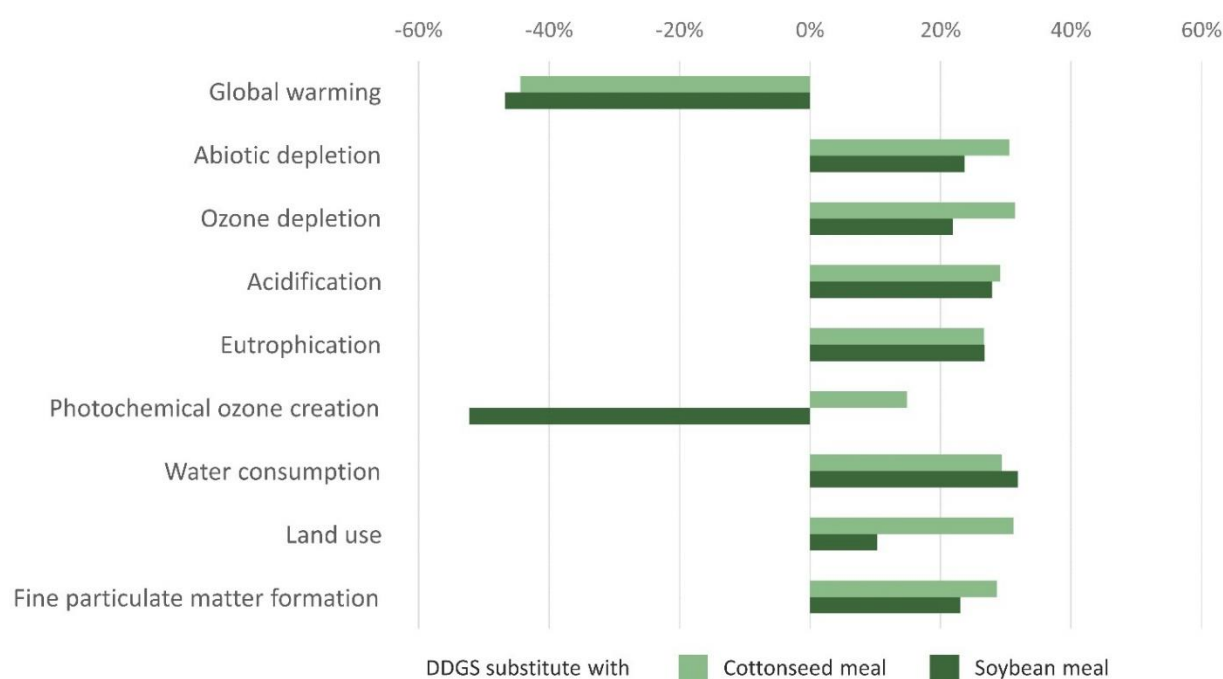


Fig. 6.6 Change in impact of bioethanol production by sorghum fermentation at all examined environmental impact categories using different cottonseed meal and soybean meal as DDGS substitute for system expansion

Without considering the POCP, the average absolute variability in using soybean meal and cottonseed meal as substitute throughout all impact categories is 27% and 30%, respectively. As mentioned before, these differences are a result of the variable quantity required to satisfy the protein content of feed and because of the specific characteristics of each seed. For example, the average yield per area for soybean is 44% and for cotton seed 81% of that of sorghum. When considering the amount of each crop to make the same protein-content feed, soybean meal requires 87% of the land associated with sorghum DDGS, while cottonseed only requires 6%. Because of using system expansion by substitution, this impact is used as an offset or credit to the entire coproducing process of sorghum fermentation. Therefore, ethanol production with soybean meal substitution is closer to the land use of the allocated reference while the cottonseed meal substitution only offsets marginally the overall fermentation process impact with its credit.



It is important to note that these results do not imply that using cottonseed or soybean meal along with the reference case will reduce the impacts in GWP or POCP. It is simply a mathematical credit in the substitution within the comparative LCA. As a system expansion without substitution, this would be equivalent to producing cottonseed or soybean meal alongside the ECCR system to use it as substitute feed to the DDGS of the sorghum bioethanol fermentation in the comparison. In that scenario, the associated impacts of producing these feed products are added to those of the ECCR system. By this perspective, cottonseed meal would be the most suitable substitute for DDGS to be used along with the ECCR system to keep impacts to a minimum.

Figure 6.7 shows the absolute impact for every environmental category using both substitute feed products along with the allocated reference process and the ECCR system at the different CI scenarios. As mentioned, the impact of sorghum bioethanol increases in all examined categories except GWP and POCP. The abiotic depletion of fossil fuels (ADP), water consumption (WC), and land use (LU) continue to be considerably higher than the ECCR at any scenario. For perspective, the reference would now require up to 81 times the water consumption and 52 times the land use of the ECCR at the Low-CI scenario. As eutrophication (EP), acidification (AP), and fine particulate matter formation (FPMF) are increased, the ECCR requires less of a reduction in this impact to break even with the reference. In contrast, the breakeven of the ECCR with the reference in GWP is decreased.

The increase in ozone depletion is marginal, but modifies the required thickness of the PTFE in the cathode to breakeven at 48  $\mu\text{m}$  and 42  $\mu\text{m}$  when using cottonseed meal and soybean meal as substitute, respectively. With respect to POCP, using cottonseed meal as substitute makes the magnitude comparable to the ECCR system at the Low-CI scenario. Using soybean meal, because of its associated hexane emissions from the solvent extraction, makes the breakeven impossible even when using the Fe-

Co anode proposed in Chapter 5. Therefore, if soybean meal were to be considered as a suitable substitute because of resources or economic reasons, it would be environmentally desirable to produce it by mechanical extraction rather than solvent extraction to make the POCP comparable to the bioethanol reference.

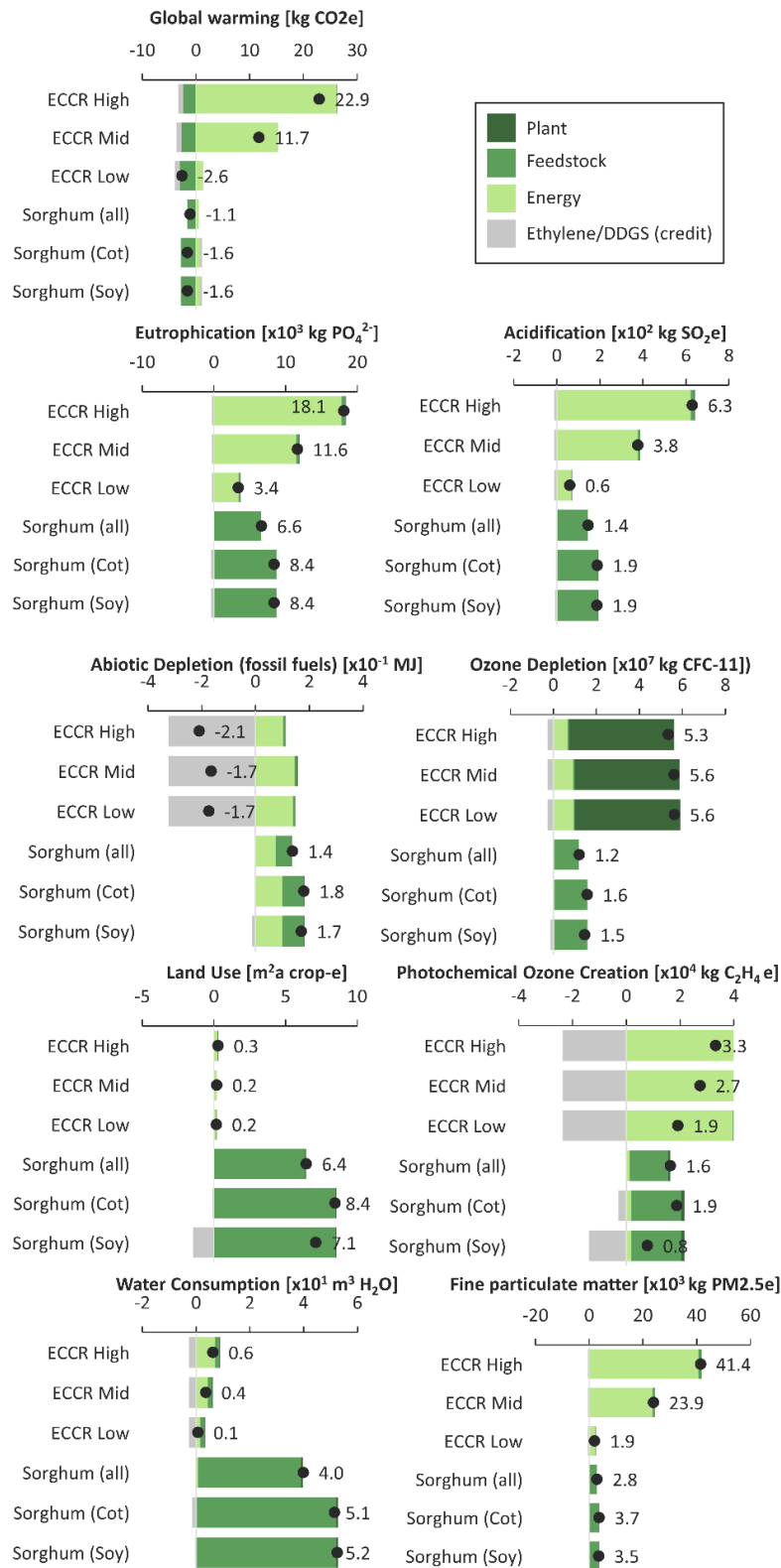


Fig. 6.7 Potential environmental impacts in all categories of the electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system at the High, Mid, and Low carbon intensity electricity scenarios and reference sorghum bioethanol system using allocation (all) and system expansion with cottonseed meal (Cot) and soybean meal (Soy)

Given the associated carbon footprint of the sorghum bioethanol decreased by 44% and 47% when using cottonseed meal and soybean meal, respectively, the sensitivity analysis on the carbon intensity of the energy provided was recalculated. Figure 6.8 shows once again the breakeven with the ECCR system. The breakeven, originally at 80 gCO<sub>2</sub>/kWh for the allocated process, would be at 63 and 62 gCO<sub>2</sub>/kWh when using system expansion with cottonseed and soybean meal respectively. This results in a variation of 21-22% in the electricity CI required to breakeven from a GWP perspective.

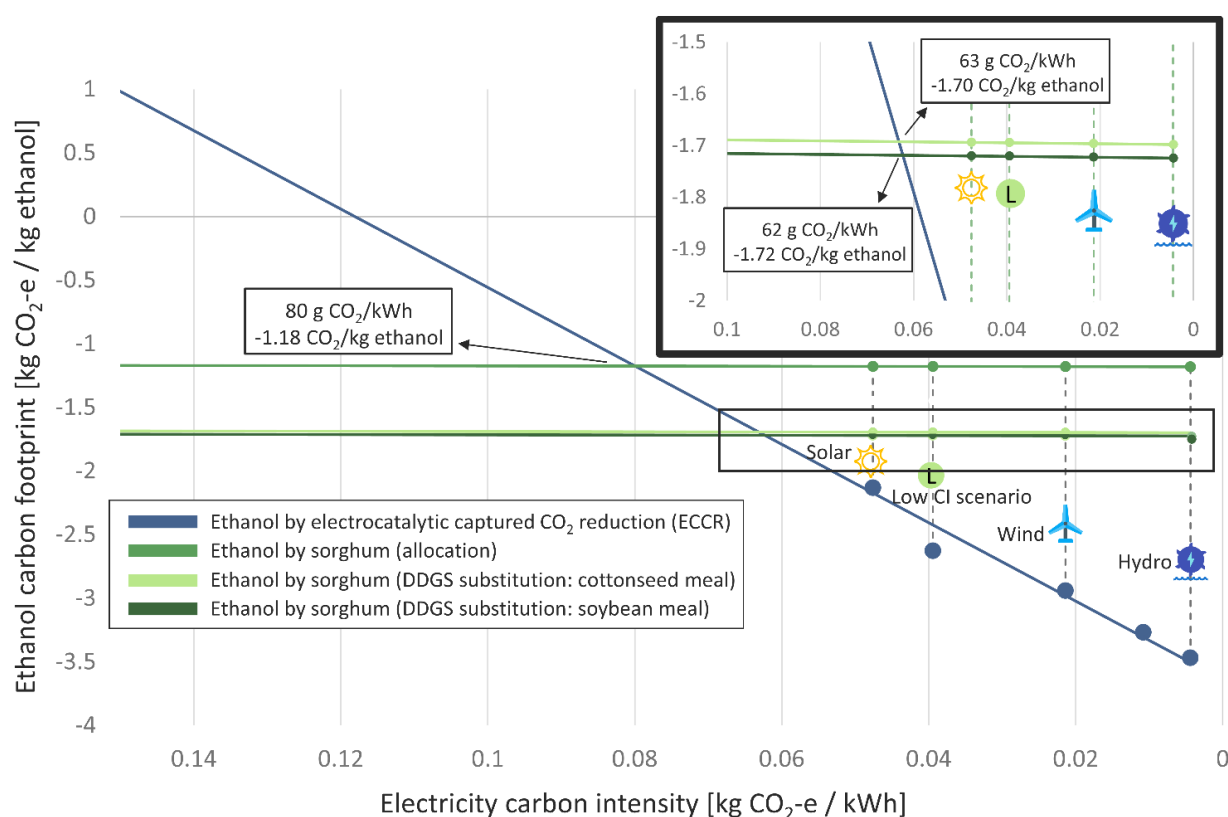


Fig. 6.8 Carbon footprint of ethanol production by electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system, by sorghum fermentation with allocation, and by sorghum fermentation with system expansion using canola meal, cottonseed meal, and soybean meal to substitute the coproduction of dry distiller's grains with solubles (DDGS), with electricity of different sources and carbon intensity. Icons taken from open-source websites [icons8.com](https://icons8.com) and [cleanpng.com](https://cleanpng.com)

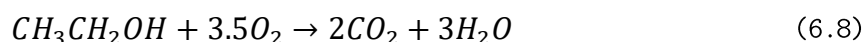
In conclusion, it is evident that using allocation or system expansion can have a perceivable effect on the impacts quantified and the conclusions obtained from the comparative assessment. The initial allocation associates a higher impact to the DDGS

than what is quantified through the equivalent substitutes. Besides the characteristics of the different seeds, the main source of variability is the increased protein content and the lower amount of meal required to satisfy its function. The particular selection of every substitute will be a function of other economic or even socio-political factors. Therefore, it is essential that the assessment includes a sensitivity analysis that can cover a feasible range of choices.

### 6.2.3.2 System boundaries

One of the most important aspects of the comparison in an LCA is that it becomes a metric to compare other processes. A variation in the selection of the system boundaries can also offer a different perspective and have an effect in the final interpretation of the results. Although the fate of ethanol is identical regardless of the process used to produce it, incorporating its combustion can serve to communicate more strongly the associated advantage of the carbon footprint of ethanol production.

As mentioned in the previous chapter, the negative GWP in the results signifies it contributes to climate change mitigation through the comparison between the two processes, but does not mean that the entire process is actually carbon negative. Being a comparative LCA, only select stages of the life cycle of ethanol in both processes are used to elaborate on its differences. In the case study, the assessment performed a cradle-to-gate approach. However, if a very simplified approach to the use phase of ethanol is included within the system boundaries, the stoichiometric emissions from its combustion can be included in the carbon footprint evaluation. While there are more associated emissions associated in the use phase of its life cycle, the emissions from combustion can be added with confidence as a quick calculation.



For the combustion of 1 kg of ethanol 95% m/m, 1.8 kg of CO<sub>2</sub> are emitted. Figure 6.9 plots the contribution of each component to GWP for the ECCR Low-CI scenario, the

sorghum reference solved by allocation and by substitution (using the average of the results of cottonseed meal and soybean meal as substitutes). Increasing those emissions to the reference by allocation at -1.1 kg CO<sub>2</sub>e results in a total GWP of 0.7 kg CO<sub>2</sub>e. For the reference by substitution, it moves from -1.6 kg CO<sub>2</sub>e to 0.2 kg CO<sub>2</sub>e. Compared to ethanol production via ECCR at the Low CI scenario, the GWP increases from -2.6 kg CO<sub>2</sub>e to -0.8 kg CO<sub>2</sub>e. While this may seem superfluous from a mathematical perspective, the assessment may draw the conclusion that sorghum bioethanol as a 1<sup>st</sup> generation biofuel can easily become carbon positive, while ethanol via the ECCR system has the potential to remain carbon neutral. In a world that is trying to be carbon neutral by 2050, the ECCR would be able to offer a long-term solution to biofuel generation.

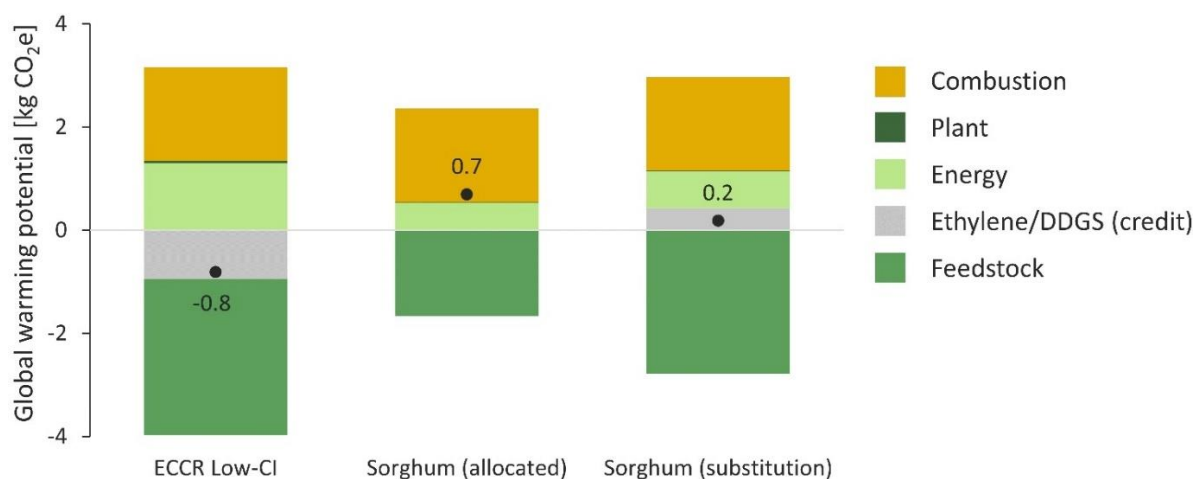


Fig. 6.9 Global warming potential of ethanol production via electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system, via sorghum fermentation modelled through allocation and substitution (using average of cottonseed meal and soybean meal results), including emissions from combustion

It is important to note how the choices of the practitioner of the assessment can have an effect on the results and conclusions. Performing a sensitivity analysis is useful in unmasking the uncertainty associated with the parameters, models, and subjective choices in the execution of the assessment. These particular parameters are also key to how the results are framed and the exact message intended to be conveyed.

In summary, the framework has inherent uncertainties that need to be accounted for and evaluated. Reductions on each type of uncertainty may be achieved by the following actions:

- Parameter uncertainty – compiling more accurate data from further investigation and first-hand processes of similar scale
- Model uncertainty – increasing the understanding and improving the analytical accuracy of the associated models to describe the natural phenomena
- Choice uncertainty – ensuring the goal and scope defined are appropriate to represent the situation and provide useful information to take a decision

Sensitivity analyses using a number of scenarios is fundamental in identifying the nature and bounds of the associated uncertainties. Practitioners and decision-makers require an account of the limitations of the assessment to elaborate suitable actionable outcomes or assess potential policies (Plevin et al. 2010). Carbon mitigation goals will require robust policies, and this framework is capable of identifying at an early-stage the areas for further focus in reducing the uncertainty where it matters most.

## 6.3 Social considerations and policy-making

Policies and carbon mitigation strategies go hand in hand with social considerations, which represent the final pillar in sustainability. Such initiatives complement techno-economic and environmental parameters with an interest to promote societal development. Additionally, the social and political context is capable of encouraging the development of technologies that may contain excessive economic risk. As Syed (2014) underlined, evidently beneficial environmental decisions, such as the reduction of fossil fuel use in electricity generation, would have been unlikely without policy initiatives.

The United Nations (UN) Sustainable Development Goals (SDGs) are an example of a global initiative to strive to more sustainable practices. After being adopted by UN members in 2015 (UN General Assembly 2015), these have now been incorporated into other public and private sector spheres. These SDGs incorporate fundamental social targets beyond those directly associated with economic and environmental justice. Government and companies have adhered to similar goals, even if they are self-imposed and flexible, such as the Science-based Targets for corporate climate action that are aligned with the level of decarbonisation needed according to the IPCC reports (Allen et al. 2018). The inclusion of metrics similar to these could be easily included in the present framework to account for all necessary parameters.

The purpose of this framework is not only to offer retrospective analysis but also to become a tool to identify future opportunities and communicate them. Framing this analytical approach around prospective strategies is helpful in comparing a range of options that best satisfy the sustainability parameters considered. These insights can become key in a multidisciplinary cooperation among relevant professionals to integrate knowledge towards policy-making.

The implementation of a proposed policy will need to account for the implications the technology can have at a community level. In the scenario of the case study, while there can be environmental benefits from a global perspective with the adoption of this new technology, there can be additional consequences to the local market. A shift in the use of sorghum for bioethanol may lead to fluctuations in price, which may affect economically the farmers in the Darling Downs area and have unintended repercussions on their lifestyle. Additionally, land not used for sorghum could be employed for other crops, depending on the nature of the specific land in the region.

Social considerations not only pertain to the benefits that CCU is able to provide to society, but also how society can be the ultimate decider in its success. As it was



concluded in the report by Dechema and VCI (2009), public acceptance of a new technology is essential to its implementation and general adoption. The use of LCA in the present framework ultimately intends to produce metrics that are comprehensible to an audience. These are able to enhance the societal perception of CCU and promote the incorporation of policies that can help in making this mechanism the norm.

### 6.3.1 Social perception of CCU

There have been substantial advances in research towards the technical and economic viability of CCU, but not much on systematic and empirical investigation in its social perception and how it might be used as a carbon mitigation mechanism (Jones 2015). Although communication to a broader audience is often overlooked in research and development, it should not be underestimated. As demonstrated by Delgado *et al.* (2011) and Terwel *et al.* (2011), inclusive engagement from the public opinion may tip the balance of the success of a new technology. While inclusive engagement has associated costs and cannot offer a guarantee, Carpini *et al.* (2004) have demonstrated that participatory strategies with a general audience have usually been met with increased trust from citizens.

A social study by Jones *et al.* (2014) indicated there is a general scepticism on the real environmental benefit of CCU, but it is widely agreed that it is an attractive method to produce valuable chemicals and fuels. This reinforces one of the main messages postulated in this thesis, which is to avoid framing CCU solely as a global warming solution but also as a mechanism capable of producing valuable chemicals while displacing the reliance of fossil fuels for manufacturing. That is one of the main advantages of CCU against carbon capture and storage (CCS). Even if developments in CCS technologies were to make coal and natural gas-fired power generation with zero emissions, the problem of fossil resource depletion is not solved. CO<sub>2</sub> is a virtually inexhaustible feedstock capable of producing a myriad of chemicals (Patil et al. 2010).

The additional emphasis on its relationship with renewable energy and its potential to be an energy vector may consolidate a general positive perception.

## 6.4 Final discussion

As it has been described throughout the entire thesis, the suitability of a CCU pathway or technology is in function of its context. The input-output analysis in Chapter 3 determines where a reduction on emissions bears the least impact on an economic and employment context. The choice of the product and technology of interest in the modelling of Chapter 4 was a result of a socio-political and environmental context. Finally, the LCA in Chapter 5 identified the benefits of the CCU technology compared to the *status quo* in terms of a geographical and technological context.

The spatial context of CCU is particularly important for a number of reasons. Firstly, the socio-economic characteristics of an economy are able to favour a specific CCU pathway. Additionally, modelling approaches such as LCA rely for their conclusions on a wide range of specific assumptions taken in the assessment, which are a function of the characteristics of a specific region. Therefore, with this method not only a suitable technology is selected according to different parameters, but also the results provide a better representation of reality. Moreover, CCU technologies are especially suitable to be located next to sources of intensive CO<sub>2</sub> emissions. Infrastructure should also be considered for ease of access to the markets of the products and the transport of the feedstock required, ensuring a minimal CO<sub>2</sub> emissions through transportation (Armstrong 2015).

The sensitivity analyses are helpful in identifying the uncertainty associated with the assessment and the effect of key variables over the system. At the same time, these analyses can uncover discrepancies according to the framing of the problem itself. As identified in this chapter, results can vary significantly when using different methods

for solving multifunctionality, which is an intrinsic problem with CCU technologies. Additionally, the specific system boundaries may contribute to the intended message conveyed.

### 6.4.1 Case study

The case study used to illustrate the proposed framework focused on ethanol production, specifically in the state of Queensland. As previously mentioned, the choice of the region of study is in function of economic, socio-political, and environmental reasons. From a socio-political perspective, Queensland has had a steady rise in biofuel production that is mainly promoted through the fuel blending mandate and the Biofutures 10-year roadmap (State of Queensland 2016). Beyond the state's agricultural capabilities, this is an example of technology driven by policy-making. As the roadmap draws to a close, it will be necessary to develop future strategies that will enable emerging technologies with high potential such as the electrocatalytic reduction of CO<sub>2</sub> presented in this work.

From an economic perspective, the preliminary analysis identified the magnitude of investment required and the associated price of electricity to make the project viable. The use of DAC for the source of CO<sub>2</sub>, although desirable from an environmental perspective, has an additional high cost associated with it compared to other sources (IEA 2020d). Therefore, this technology may only be economically viable if it is supported by a significant carbon credit. From the IOA results in Chapter 3, the lowest GDP loss when considering only a CO<sub>2</sub> reduction in Agriculture is \$120 USD/tonne CO<sub>2</sub>e. This value is consistent with the magnitude of carbon price projected, indicating not only that the credit can safely be valued at that amount, but also that the framework can be helpful as a tool for prospective policy-making.

From an environmental perspective, the LCA examined in detail the potential benefits in the comparison of the proposed ECCR system against sorghum

fermentation, which is the industry reference in the area of study. Being highly sensitive to the nature of the energy supplied to power the system, the ECCR presents improved or comparable in almost all of the examined environmental impact categories. Additionally, the assessment identified areas for improvement in the proposed system. The POCP and ODP are the only impact categories that require further attention from a materials perspective to ensure they are comparable to the reference. Chapter 5 proposed potential solutions, including using a different catalyst for the anode and a reduced thickness of PTFE layer in the catalyst for the cathode. Using an anode based on a Fe-Co film on carbon fibre paper as the one characterised by Liu *et al.* (2017) show a significant reduction on POCP and a potential decrease in the energy requirements. However, future experimentation is required to confirm its improved performance. Similarly, if this technology is to be competitive with its current use of PTFE, its manufacture will require to reduce the associated CFC emissions or the CO<sub>2</sub> reduction catalyst should consider using a substitute material.

A number of sensitivity analyses are able to prove the validity of the interpretation of the LCA results. Differences in the assumptions of the proposed system or the reference itself can have significant variations in the results. Chapter 5 identified the difference of assuming different sources for the sorghum used for fermentation, depending on whether it came from dryland or irrigated sources. One other important factor is the industry reference for the avoided ethylene that is co-produced by the ECCR system. As its inventory in Appendix B details, this process represents the current practice by Qenos in olefins production near the area of study. However, future developments in cleaner practices such as using electric furnaces for cracking ethane for ethylene production will impact directly the credit associated with the ECCR system. Being reliant on the nature of the energy supplied, the credit would decrease proportionally through the electricity generation scenarios. Although electric

cracking furnaces are still in the development phase (Ondrey 2020), this reinforces the need to update assessments to ensure they provide a reliable representation of reality.

Furthermore, the credit of the ethylene is meaningful in determining the impact of the overall system. Specifically for this GWP quantification, it reduces the carbon footprint further in its comparison to sorghum bioethanol. If the ECCR were to produce a different chemical than ethylene, its overall impact would be modified. Therefore, besides the technical differences in the specific separation process required in the system, the type of by-product of the ECCR will become a key consideration in its environmental and economic assessment.

Finally, from an energy point of view, the process proves to be energy-intensive but highly suitable to be used as a vector for surplus renewable energy. The LCA proved the process provides a benefit when it employs a high share of renewable energy or a single source of them. Being a modular and easily scalable system, it can be installed next to a source of renewable energy and take advantage of it. These can also be remote areas where there are no transmission networks. Storing and transporting ethanol and ethylene can leverage existing infrastructure. Specifically for ethanol, avoiding the need of agricultural resources and land has the ability to support the biofuels industry while reducing its interrelated uncertainty in the market and increasing the fuel stability of the state. Naturally, land may be required for renewable energy generation, but it does not need to compete with arable land.

It is important to mention this process does not intend to substitute altogether the fermentation of crops for bioethanol production. The fermentation of sorghum, as a 1<sup>st</sup> generation biofuel, is helpful in promoting agricultural trade, the production of ethanol, and the coproduction of a high-protein feed used directly in the area of study. As mentioned in the discussion of Chapter 5, there is even an opportunity of integrating the ECCR to a fermentation plant to increase the total bioethanol production. This integration can be useful in areas where agricultural resources are available. Therefore,

the electrochemical conversion does not intend to remove any existing process in ethanol production but offer a new path with inherent advantages in what can be coined as 5<sup>th</sup> generation biofuel generation.

## 6.4.2 Scaling

Appropriate scaling of a technology can be challenging, especially when it has a low TRL. Chapter 5 mentioned key parameters to test in the prospective scaling of the case study. Usually, there can be resource limitations to the materials required to manufacture novel technologies. Specifically in the CCU system of the case study, none of the materials used are precious or are available in low quantities. However, preliminary analyses of availability and requirements in key materials used in a study can be an effective guidance in the development of new technologies (Sathre et al. 2012).

Besides the technical challenge of increasing the performance of the technology at a scale beyond laboratory, processes with a low TRL may not scale-up in the same pattern as they are modelled in an assessment. However, as Brennan (1992) reviewed, economies of scale may play a positive role in the further optimisation of the process. Therefore, estimating the environmental performance of future technologies at a large or global industrial scale is difficult and subject to uncertainty. The operational configuration of the actual scaled process may bring structural changes that have a repercussion in the assessment and the potential environmental impact obtained.

Moreover, when the technology reaches a widespread large-scale application and the repercussions become relevant at a regional or global scale, the analytical approach should follow the same resolution. For example, extra ethanol produced by a single ECCR system would only be perceived as a marginal change in the ethanol availability in the region. However, as this technology is adopted at a larger scale

worldwide, the entire ethanol production and biofuels subsystems would shift, bringing a structural change in the food-water-energy nexus (Bellezoni et al. 2018).

Such significant structural changes or market fluctuations influenced by external factors in the implementation of any new technology are difficult to grasp solely by sensitivity and scenario analysis. Policies and market changes can create a significant variation in the future scenarios assumed. In order to model how other tiers in the system can react, complementary modelling approaches with increased system boundaries and considerations can help in measuring the dynamic nature of the variables in the system. Examples of these complementary approaches are provided in the Future work section of Chapter 7.

## 6.5 Conclusions

This discussion chapter readdressed the necessary components of sustainability and how they relate to the framework and case study employed. The preliminary economic analysis gauged the magnitude of capital costs and total cost of equipment according to the price of electricity. This evaluation indicates the economic viability of the ECCR system is within range, relying on carbon credit from captured CO<sub>2</sub> to offset the associated costs. Then, the uncertainty analysis discussed relevant aspects in testing the validity of the interpretation of the LCA results and offered recommendations on how to reduce uncertainty. Specifically for the case study, using a 20-year and 100-year horizon for the calculation of the GWP does not have a significant effect. However, solving the multifunctionality of the reference system by allocation or by substitution does create a substantial difference in the comparative assessment. Moreover, increasing the system boundaries to account for the combustion of ethanol exemplifies the effect of the conveyed message. From that analysis, the potential for ethanol production via ECCR to become a carbon-neutral and long-term solution to biofuel

generation is reinforced. Finally, the social considerations discuss the particular effect that this technology might develop and the importance of social perception to the ultimate success of the adoption of a new technology.

The specific results and discussion show that this technology has great potential to produce ethanol as a CCU mechanism. The sensitivity analysis proved the ECCR system is capable of offering environmental benefits or comparable performance in all examined impact categories according to particular conditions. An understanding of the associated uncertainty is helpful to identify areas for improvement in the assessment and strengthen the representativeness of the conclusions. Even though the reference was modelled with geographical specifications for Queensland, the assessment and discussion are relevant to global bioethanol production from crops. With a significantly reduced land footprint and water consumption, this system may prove to be useful as a 5<sup>th</sup> generation biofuel process that does not require agricultural resources and acts as a renewable energy vector. These findings are significant because, while this technology is not mature enough to meet the proposed scale, it proves that this is a promising pathway that can not only offer the benefits associated with carbon capture and utilisation but also present an alternative in sustainable bioenergy production.



# 7 Conclusions and recommendations for future work

Despite numerous technical publications on novel processes and environmental analyses for individual technologies, there remain significant gaps in the selection of a CCU pathway suitable for a specific region to determine its sustainable application. At present time, even though there are guidelines for methodological considerations, there is no single framework that incorporates multiple methods for rigorous assessment and decision-making.

This research project fills such a gap by providing a systematic method to select and analyse a suitable CCU technology in a particular region. The proposed framework provides a complete assessment on CCU, considering the technical feasibility of the processes, the specific socio-economic considerations of the region, and the environmental impacts of its implementation.

## 7.1 Contributions of research

The main contribution in this research is the proposed general framework that facilitates the selection and evaluation of CCU technologies that can best reduce environmental impacts in its sustainable application according to the specific configuration of a region. This single systematic framework is based on existing methodological approaches tailored for CCU assessment that can be applied globally.

The extended input-output analysis (IOA) model can analyse the specific configuration of a regional economy, including associated environmental and socio-economic properties of every sector. It quantifies the difference of emissions

responsibility in sectors according to a producer or consumer perspective, providing an insight to the structure of emissions in the regional economy. The innovative integration with multi-objective optimisation (MOO) is a quick and mechanistic method to map a scenario of emissions reductions with minimal effect on the extended parameters selected, determining the sectors for further focus. At the time of the publication of Rojas Sanchez *et al.* (2019), this was the first extended IOA model that supported multiple objectives in the optimisation framework.

The methodology demonstrates the capability of modelling techniques paired with mathematical optimisation algorithms to extract insights from publicly-available national accounts data. Additionally, the model is an innovative contribution on its own. Because of its adjustable and scalable configuration, the model allows multiple objective functions, providing an optimal solution that considers as many socio-economic and environmental parameters as required. As a stand-alone tool, it is capable of screening the overall consequences of policies that regulate sectors or environmental considerations and can serve as the basis for future tailored analysis.

The elaboration of the inventory of the life cycle assessment (LCA) provides a guideline to approach CCU technologies with a low technology readiness level (TRL). Future practitioners may refer to the process modelling, simulations, and heat integration in this work to create an integrated system that considers key auxiliary components of the system, such as product separation or purification. The optimisation of existing systems in combination with emerging processes is critical since it reduces the energy requirements of these energy-intensive stages (Dechema & VCI 2009). Considerations on scaling to a relevant magnitude are subject to substantial uncertainty and should be handled with similar care.

The LCA aids in mapping the structural path of environmental stressors along the chain, showing key sections for improvement. Moreover, it can effectively quantify the indirect energy and emissions savings of a particular pathway when substituted for

the industrial benchmark, thus allowing a real comparison of the benefits of CCU. The main advantage of the approach with early-stage technologies is identifying areas for improvement and further focus. The sensitivity analysis, especially in solving the multifunctionality of the systems, is capable of reinforcing the representativeness of the results.

This study confirms that, despite the existence of LCA guidelines for CCU, there is a persistent methodological ambiguity in solving the multifunctionality of CCU pathways. The case study demonstrates how this uncertainty can lead to significant differences in the results of the assessment. Additionally, the application of the framework is unique since the reference used in the comparative assessment is bio-based. Existing LCA guidelines focus on the methodology to compare a CCU system against a fossil-based reference. However, substantial changes in production and consumption activities will gradually phase out fossil fuels until they become obsolete. The present framework then sets the basis for future comparison with non-fossil-based processes to assess non-evident benefits of CCU systems in the long term.

In terms of the geographical focus and spatial resolution, the benefits of the framework are two-fold. Firstly, the selection of a CCU technology is a function of the specific socio-economic and environmental parameters of a region, ensuring it will be directed to where it is most efficient. Secondly, the assumptions and conditions are characteristic of the location of study, so the results are able to provide a better representation of the real impacts.

The results and discussion of the entire framework set the precedent to create carbon utilisation strategies for a region or match existing technologies to the most suitable location. This can consequently promote further research and development for specific technologies. Future sustainability roadmaps can be supported through analyses performed through this framework, being capable of identifying at an early-stage the areas for further focus in reducing the uncertainty where it matters most.

## 7.2 Case study conclusions

The efficacy of the proposed framework is demonstrated through the case study application. It is useful in illustrating the objective and robust capability of the methodology in identifying benefits from an early-stage CCU technology that are not evident from an initial perspective. To my knowledge, this is the first study in the literature to perform a comprehensive environmental assessment on large-scale ethanol production using this technology in an entire production plant.

The extended IOA model showed a significant difference in the allocation of emissions to sectors as producers or consumers, indicating that the Australian economy has a small number of emissions-intensive sectors from which many other sectors rely on for their activities. Then, the MOO mapped a solution space where the sectors with the optimal potential to reduce emissions with the least impact on gross domestic product and employment are agriculture and power supply.

The conceptual process design of the electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system allows using an existing electrolyser with proven potential for ethanol and ethylene coproduction through the integration with a novel product separation system. The proposed design maximises separation with minimal losses by recirculating unreacted CO<sub>2</sub> in an efficient and heat-integrated configuration.

The modelling of a fully-electric process is capable of underpinning the benefits of renewable energy. The LCA proves the ECCR system can offer comparable or improved impacts in all the examined environmental categories depending on the carbon intensity of the electricity used and the materials used in the electrodes. Being electricity-intensive, the system is highly sensitive to the nature of the electricity used to power it. From a global warming perspective, the ECCR becomes competitive with the reference process when the electricity supplied to the system has a carbon intensity

of 80 gCO<sub>2e</sub> per kWh. Therefore, this process becomes competitive when powered by renewable energy directly or a grid that has a high share of renewable sources.

Although the main contribution to most environmental categories is the energy supplied, the analysis quantified considerable impacts from the manufacturing of the electrodes. The case study illustrates the importance of including embodied emissions in the manufacture of the components of the plant through comprehensive inventories and not relying solely on operational flowsheet information. This is also applicable to the materials used in renewable energy infrastructure. As the framework was capable of identifying such hotspots and propose potential improvements, this approach should be included in all future assessments when using emerging CCU technologies.

The effect of the coproducts in both the proposed CCU system and the reference are considerable. The substitution credit for the coproduction of ethylene is essential to have a lower impact in abiotic depletion of fossil fuels than the reference. Additional sensitivity analyses indicate that the environmental impacts of the reference make a considerable difference when the feed coproduct of the fermentation is solved by substitution rather than allocation. Besides a decrease in global warming and thus a lower breakeven carbon intensity of the electricity (62-63 gCO<sub>2e</sub>/kWh), all the other environmental impacts of the reference increase, making the ECCR system more attractive in comparison.

The preliminary economic evaluation indicates the total cost of equipment is within a feasible range in terms of historical prices and projections. The use of direct air capture increases the economic risk but also justifies a carbon credit, which is able to offset the associated costs. Whilst the economic analysis is only preliminary, it indicates that the system is likely to be viable. From a socio-political perspective, the region of study is likely to support additional ethanol production but may not be in a position to supply it from agriculture as it has done in the past. The development of this technology is able to promote future policies as the next generation of bioethanol.

The case study illustrates the feasibility and importance of using CO<sub>2</sub> from the air in positioning the process as a long-term prospect rather than a transition technology linked to fossil fuels. The main benefit lies in only requiring waste CO<sub>2</sub> from the atmosphere as a virtually inexhaustible feedstock. Specifically for the ECCR, it is a modular system that has a substantially lower water and land footprint, proving to be useful in regions where agricultural resources are unavailable. It can also be positioned next to sources of renewable energy to utilise surplus electricity and act as a renewable energy vector. This is practical for isolated areas without transmission networks in Queensland and Australia overall, decentralising and increasing the security of the energy and fuel supply system in the country. Since this technology avoids the burden of agricultural subsystems, it is a potential carbon-neutral and long-term solution to sustainable bioenergy generation.

Finally, this study demonstrates the relevance of evaluating the potential of early-stage technologies, determining the likely impacts at a relevant magnitude and identifying the areas for further focus. Being a low TRL process, the design has yet to reach a magnitude that has industrial relevance. The case study assumed that the electrode size can be scaled to a commercially-relevant magnitude and has a stable continuous operation of 5,000 hours. As the technology continues its development pathway, the overall CCU pathway would require revisiting the assessment.

## 7.3 Future work

Since the nature of the framework builds on an array of methodologies in succession, there is a great potential for further development. The present framework sets the foundation upon which other assessments can be incorporated to further the analysis of the associated overall impacts. As mentioned in Chapter 6, complementary

modelling approaches can estimate market fluctuations and significant structural changes resulting from the implementation of the CCU mechanism.

A consequential LCA can be further performed to quantify the potential effect of the introduction of the technology in the market. The attributional LCA in the current framework is critical as a first screening to identify opportunities and validate the potential environmental benefits against the benchmark. Once it shows a benefit, the framework can later incorporate a consequential LCA to evaluate the effect of the demand of the technology or its role in larger policy-making interests at a systems level (Earles & Halog 2011). This information can be combined as an extra tier in estimating the consequence of prospective decisions and determining the region's specific suitability to incorporate the CCU pathway.

Similarly, there is potential for convergence with other more robust economic modelling approaches. For instance, computable general equilibrium models also quantify indirect impacts but provide a more rigorous control over the variables of the entire economic system and the non-linear consequences of a perturbation over it (Zhou et al. 2018). They can account more accurately for marginal energy and material flows impacts while incorporating rebound effects (Xie & Saltzman 2000), which are limitations of the current input-output model. In the context of the case study, the repercussions of a global adoption of the technology could affect ethanol prices and the current market of crop feedstock, which could in turn shift the trade and employment in agricultural regions.

While these modelling approaches can be beneficial complements, the analysis described in the proposed framework is critical to be performed beforehand. As Sathre *et al.* (2012) concluded, increased system boundaries and uncertainties associated with market effects can make the assessment inefficient to draw practical recommendations for the CCU system itself, especially when dealing with emerging technologies. Future development may increase the capabilities of the framework to evaluate the specific

TRL of a CCU technology and fit the scope of analysis to their respective stage characteristics.

The identification of key parameters within the system can offer valuable information with which potential scenarios can be evaluated. The framework additionally allows targeting areas of improvement or further scrutiny. Complementary modelling approaches will be then useful to deepen the understanding of the specific outcomes of the implementation. These additional analytical tools will require a combined approach from professionals of multiple disciplines.

CCU will need to be implemented globally at a large scale in order to be an effective mechanism against climate change. A systematic assessment framework such as the one presented in this research provides a better understanding of the widespread application of CCU, representing a step forward in the complex path towards building a sustainable anthropogenic carbon cycle.



# References

- Abdin, Z, Zafaranloo, A, Rafiee, A, Merida, W, Lipinski, W, & Khalilpour, KR 2019, 'Hydrogen as an energy vector' *Renewable and Sustainable Energy Reviews*, no. December.
- ABS 2006, *Australian and New Zealand Standard Industrial Classification (ANZSIC) Australian Bureau of Statistics, Catalogue No. 1292.0 (Rev. 2)*, doi:/ABS Catalogue No. 1292.0.
- Adams, TA, Hoseinzade, L, Madabhushi, PB, & Okeke, IJ 2017, 'Comparison of CO<sub>2</sub> capture approaches for fossil-based power generation: Review and meta-study' *Processes*, vol. 5, no. 3.
- Adanez, J, Abad, A, Garcia-Labiano, F, Gayan, P, & de Diego, LF 2012, 'Progress in Chemical-Looping Combustion and Reforming technologies' *Progress in Energy and Combustion Science*, vol. 38, no. 2, pp. 215–282.
- AEMO 2021, 'Queensland Annual Average Price', NEM Data Dashboard, viewed 8 April 2021, <https://aemo.com.au/en/energy-systems/electricity/national-electricity-market-nem/data-nem/data-dashboard-nem>.
- Agarwal, AS, Zhai, Y, Hill, D, & Sridhar, N 2011, 'The electrochemical reduction of carbon dioxide to formate/formic acid: Engineering and economic feasibility' *ChemSusChem*, vol. 4, no. 9, pp. 1301–1310.
- Ager, JW & Lapkin, AA 2018, 'Chemical storage of renewable energy' *Science*, vol. 360, no. 6390, pp. 707–708.
- Ahmed, NSE & El-Shishtawy, RM 2010, 'The use of new technologies in coloration of textile fibers' *Journal of Materials Science*, vol. 45, no. 5, pp. 1143–1153.
- AIB 2020, *European Residual Mixes 2019*.
- Al-Kalbani, H, Xuan, J, García, S, & Wang, H 2016, 'Comparative energetic assessment of methanol production from CO<sub>2</sub>: Chemical versus electrochemical process' *Applied Energy*, vol. 165, pp. 1–13.
- Al-musleh, EI, Mallapragada, DS, & Agrawal, R 2014, 'Continuous power supply from a baseload renewable power plant' *Applied Energy*, vol. 122, pp. 83–93.
- Allen, M, Babiker, M, Chen, Y, Coninck, H de, Connors, S, Diemen, R van, Dube, OP, Ebi, K, Engelbrecht, F, Ferrat, M, Ford, J, Forster, P, Fuss, S, Guillen, T, Harold, Jo, Hoegh-Guldberg, O, Hourcade, J-C, Huppmann, D, Jacob, D, Jiang, K, Johansen, TG, Kainuma, M, & Kleijne, K de 2018, 'Summary for Policymakers' in *IPCC Special Report Global Warming of 1.5°C*, p. 33.
- Alper, E & Yuksel Orhan, O 2017, 'CO<sub>2</sub>utilization: Developments in conversion processes' *Petroleum*, vol. 3, no. 1, pp. 109–126.
- Amos, P, Louis, H, Adesina Adegoke, K, Eno, EA, Udochukwu, AO, & Odey Magub, T 2018, 'Understanding the Mechanism of Electrochemical Reduction of CO<sub>2</sub> Using Cu/Cu-Based Electrodes: A Review' *Asian Journal of Nanoscience and Materials*, vol. 1, no. 4, pp. 183–224.
- Ang, RR, Sin, LT, Bee, ST, Tee, TT, Kadhum, AAH, Rahmat, AR, & Wasmi, BA 2015, 'A review of copolymerization of green house gas carbon dioxide and oxiranes to produce polycarbonate' *Journal of Cleaner Production*, vol. 102, pp. 1–17.
- Aresta, M 1999, 'Perspectives in the use of carbon dioxide' *Química Nova*, vol. 22, no. 2, pp. 269–272.
- Aresta, M 2006, 'Carbon Dioxide Reduction and Uses as a Chemical Feedstock' in *Activation of Small Molecules: Organometallic and Bioinorganic Perspectives*, pp. 1–41.
- Aresta, M 2010, *Carbon Dioxide as Chemical Feedstock* ed. M. Aresta, *Carbon Dioxide as Chemical*

*Feedstock*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

- Aresta, M, Caroppo, A, Dibenedetto, A, & Narracci, M 2002, 'Life Cycle Assessment (LCA) applied to the synthesis of methanol. Comparison of the use of syngas with the use of CO<sub>2</sub> and dihydrogen produced from renewables' in M. M. Maroto-Valer, C. Song, & Y. Soong (eds.), *Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century*, 1st edn, pp. 331–347, Springer, New York.
- Aresta, M, Dibenedetto, A, & Angelini, A 2013, 'The changing paradigm in CO<sub>2</sub> utilization' *Journal of CO<sub>2</sub> Utilization*, vol. 3–4, pp. 65–73.
- Aresta, M, Dibenedetto, A, & Angelini, A 2014, 'Catalysis for the valorization of exhaust carbon: From CO<sub>2</sub> to chemicals, materials, and fuels. technological use of CO<sub>2</sub>' *Chemical Reviews*, vol. 114, no. 3, pp. 1709–1742.
- Aresta, M, Dibenedetto, A, & Quaranta, E 2016, 'State of the art and perspectives in catalytic processes for CO<sub>2</sub> conversion into chemicals and fuels: The distinctive contribution of chemical catalysis and biotechnology' *Journal of Catalysis*, vol. 343, pp. 2–45.
- Armstrong, K 2015, 'Chapter 13 - Emerging Industrial Applications' in P. Styring, E. A. Quadrelli, & K. Armstrong (eds.), *Carbon Dioxide Utilisation*, pp. 237–251, Elsevier, Amsterdam.
- Arnold, DS, Barrett, DA, & Isom, RH 1982, 'CO<sub>2</sub> Can be Produced from Flue Gas' *Oil Gas J.*, vol. 80, no. 47.
- Artz, J, Müller, TE, Thenert, K, Kleinekorte, J, Meys, R, Sternberg, A, Bardow, A, & Leitner, W 2018, 'Sustainable Conversion of Carbon Dioxide: An Integrated Review of Catalysis and Life Cycle Assessment' *Chemical Reviews*, vol. 118, no. 2, pp. 434–504.
- Assen, N von der, Müller, LJ, Steingrube, A, Voll, P, & Bardow, A 2016, 'Selecting CO<sub>2</sub> Sources for CO<sub>2</sub> Utilization by Environmental-Merit-Order Curves' *Environmental Science & Technology*, vol. 50, no. 3, pp. 1093–1101.
- Atsonios, K, Panopoulos, KD, & Kakaras, E 2016, 'Thermocatalytic CO<sub>2</sub> hydrogenation for methanol and ethanol production: Process improvements' *International Journal of Hydrogen Energy*, vol. 41, no. 2, pp. 792–806.
- Atti-Santos, AC, Rossato, M, Serafini, LA, Cassel, E, & Moyna, P 2005, 'Extraction of essential oils from lime (*Citrus latifolia* tanaka) by hydrodistillation and supercritical carbon dioxide' *Brazilian Archives of Biology and Technology*.
- Australian Academy of Science 2021, *The risks to Australia of a 3C warmer world*.
- Australian Department of the Environment 2012, 'National Greenhouse Gas Inventory', Australia's National Greenhouse Accounts, viewed 18 November 2018, <http://ageis.climatechange.gov.au/>.
- Australian Energy Market Operator 2020a, *2020 Integrated System Plan*.
- Australian Energy Market Operator 2020b, *Carbon Dioxide Equivalent Intensity Index*.
- Australian Life Cycle Assessment Society 2020, 'Australian Life Cycle Initiative Database V1.35'.
- Aydin, G, Karakurt, I, & Aydinler, K 2010, 'Evaluation of geologic storage options of CO<sub>2</sub>: Applicability, cost, storage capacity and safety' *Energy Policy*, vol. 38, no. 9, pp. 5072–5080.
- Balat, M & Balat, H 2009, 'Recent trends in global production and utilization of bio-ethanol fuel' *Applied Energy*, vol. 86, no. 11, pp. 2273–2282.
- BASF Venture Capital GmbH n.d., 'LanzaTech Inc', Portfolio, viewed 26 February 2021, [https://www.basf.com/global/en/who-we-are/organization/group-companies/BASF\\_Venture-Capital/portfolio/LanzaTech-Inc.html](https://www.basf.com/global/en/who-we-are/organization/group-companies/BASF_Venture-Capital/portfolio/LanzaTech-Inc.html).

- Baxter, T 2017, August, 'It's time to accept carbon capture has failed – here's what we should do instead' *The Conversation*, pp. 1–5.
- Beccali, M, Cellura, M, Longo, S, Finocchiaro, P, & Selke, T 2014, *IEA Report on LCA*.
- Bellezoni, RA, Sharma, D, Villela, AA, & Pereira Junior, AO 2018, 'Water-energy-food nexus of sugarcane ethanol production in the state of Goiás, Brazil: An analysis with regional input-output matrix' *Biomass and Bioenergy*, vol. 115, no. May, pp. 108–119.
- Benson, HP 1998a, 'An Outer Approximation Algorithm for Generating All Efficient Extreme Points in the Outcome Set of a Multiple Objective Linear Programming Problem' *Journal of Global Optimization*, vol. 13, no. 1, pp. 1–24.
- Benson, HP 1998b, 'Further Analysis of an Outcome Set-Based Algorithm for Multiple-Objective Linear Programming' *Journal of Optimization Theory and Applications*, vol. 97, no. 1, pp. 1–10.
- Bertilsson, F & Karlsson, HT 1996, 'CO2 utilization options, Part I: An emission assessment framework' *Energy Conversion and Management*, vol. 37, no. 12, pp. 1725–1731.
- Bertuccioli, L, Chan, A, Hart, D, Lehner, F, Madden, B, & Standen, E 2014, *Development of water electrolysis in the European Union Fuel Cells and Hydrogen Joint Undertaking*.
- Blom, MJW, van Swaaij, WPM, Mul, G, & Kersten, SRA 2019, 'Overall mass balance evaluation of electrochemical reactors: The case of CO2 reduction' *Electrochimica Acta*, vol. 333, p. 135460.
- BloombergNEF 2019, *Hydrogen: The economics of production from renewables*.
- Boot-Handford, ME, Abanades, JC, Anthony, EJ, Blunt, MJ, Brandani, S, Mac Dowell, N, Fernández, JR, Ferrari, M-C, Gross, R, Hallett, JP, Haszeldine, RS, Heptonstall, P, Lyngfelt, A, Makuch, Z, Mangano, E, Porter, RTJ, Pourkashanian, M, Rochelle, GT, Shah, N, Yao, JG, & Fennell, PS 2014, 'Carbon capture and storage update' *Energy Environ. Sci.*, vol. 7, no. 1, pp. 130–189.
- Bozzano, G & Manenti, F 2016, 'Efficient methanol synthesis: Perspectives, technologies and optimization strategies' *Progress in Energy and Combustion Science*, vol. 56, pp. 71–105.
- Branson, R 2018, 'Virgin Atlantic flies the first ever commercial flight using LanzaTech's sustainable jet fuel', Richard Branson's Blog, viewed 26 February 2021, <https://www.virgin.com/branson-family/richard-branson-blog/virgin-atlantic-flies-first-ever-commercial-flight-using-lanzatechs-sustainable-jet>.
- Brennan, DJ 1992, 'Evaluating scale economies in process plants: a review' *Chemical Engineering Research and Design*, vol. 70, pp. 516–526.
- Brennan, DJ 2002, 'Scale-up or Scale-out?' in I. Wichterle (ed.), *CHISA 2002*, Czech Society of Chemical Engineering.
- Brookes, L 1990, 'Energy efficiency and economic fallacies' *Energy Policy*, pp. 783–785.
- Bruce, SL 2013, *Ethanol Supply Chain and Industry Overview: More Harm Than Good?*, masters thesis, Massachusetts Institute of Technology.
- Brunner, G 2005, 'Supercritical fluids: technology and application to food processing' *Journal of Food Engineering*, vol. 67, no. 1–2, pp. 21–33.
- Bryden, WL, Selle, PH, Cadogan, DJ, Li, X, Muller, ND, Jordan, DR, Gidley, MJ, & Hamilton, WD 2009, *A Review of the Nutritive Value of Sorghum for Broilers*.
- BSI 2011, *PAS 2050:2011 Specification for the assessment of the life cycle greenhouse gas emissions of goods and services*. British Standards Institution, London.
- Bui, M, Adjiman, CS, Bardow, A, Anthony, EJ, Boston, A, Brown, S, Fennell, PS, Fuss, S, Galindo, A, Hackett, LA, Hallett, JP, Herzog, HJ, Jackson, G, Kemper, J, Krevor, S, Maitland, GC, Matuszewski,

- M, Metcalfe, IS, Petit, C, Puxty, G, Reimer, J, Reiner, DM, Rubin, ES, Scott, SA, Shah, N, Smit, B, Trusler, JPM, Webley, P, Wilcox, J, & Mac Dowell, N 2018, 'Carbon capture and storage (CCS): The way forward' *Energy and Environmental Science*, vol. 11, no. 5, pp. 1062–1176.
- Burdyny, T & Smith, WA 2019, 'CO<sub>2</sub> reduction on gas-diffusion electrodes and why catalytic performance must be assessed at commercially-relevant conditions' *Energy and Environmental Science*, vol. 12, no. 5, pp. 1442–1453.
- 'Calera' n.d., viewed 18 October 2018, <http://www.calera.com>.
- Calix Limited n.d., 'Our Technology', viewed 26 February 2021, <https://www.calix.global/our-technology/>.
- Cao, M, Zhao, L, Xu, D, Ciora, R, Liu, PKT, Manousiouthakis, VI, & Tsotsis, TT 2020, 'A carbon molecular sieve membrane-based reactive separation process for pre-combustion CO<sub>2</sub> capture' *Journal of Membrane Science*, vol. 605, p. 118028.
- Cao, Y, Casenas, B, & Pan, W-P 2006, 'Investigation of Chemical Looping Combustion by Solid Fuels. 2. Redox Reaction Kinetics and Product Characterization with Coal, Biomass, and Solid Waste as Solid Fuels and CuO as an Oxygen Carrier' *Energy & Fuels*, vol. 20, no. 5, pp. 1845–1854.
- 'Carbon Recycling International' n.d., viewed 15 October 2018, <http://www.carbonrecycling.is>.
- 'Carbon8' n.d., viewed 19 October 2018, <http://c8s.co.uk>.
- CarbonCure Technologies 2020, *CarbonCure's Path to the Decarbonization of Concrete*.
- Carmo, M, Fritz, DL, Mergel, J, & Stolten, D 2013, 'A comprehensive review on PEM water electrolysis' *International Journal of Hydrogen Energy*, vol. 38, no. 12, pp. 4901–4934.
- Carpini, MXD, Cook, FL, & Jacobs, LR 2004, 'Public deliberation, discursive participation, and citizen engagement: A review of the empirical literature' *Annual Review of Political Science*, vol. 7, no. 1, pp. 315–344.
- Casas, N, Schell, J, Pini, R, & Mazzotti, M 2012, 'Fixed bed adsorption of CO<sub>2</sub>/H<sub>2</sub> mixtures on activated carbon: Experiments and modeling' *Adsorption*, vol. 18, no. 2, pp. 143–161.
- Centi, G & Perathoner, S 2010, 'Towards Solar Fuels from Water and CO<sub>2</sub>' *ChemSusChem*, vol. 3, no. 2, pp. 195–208.
- Centi, G & Perathoner, S 2011, 'CO<sub>2</sub>-based energy vectors for the storage of solar energy' *Greenhouse Gases: Science and Technology*, vol. 1, no. 1, pp. 21–35.
- Centi, G, Quadrelli, EA, & Perathoner, S 2013, 'Catalysis for CO<sub>2</sub> conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries' *Energy & Environmental Science*, vol. 6, no. 6, pp. 1711–1731.
- Chang, H, Li, Q, Cui, X, Wang, H, Bu, Z, Qiao, C, & Lin, T 2018, 'Conversion of carbon dioxide into cyclic carbonates using wool powder-KI as catalyst' *Journal of CO<sub>2</sub> Utilization*, vol. 24, no. November 2017, pp. 174–179.
- Chang, J 2016, 'Covestro Co<sub>2</sub>-based plant to start up in June', ICIS News, viewed 18 October 2018, <https://www.icis.com/resources/news/2016/04/07/9986126/corrected-covestro-co2-based-plant-to-start-up-in-june/>.
- Chaudhari, NK, Jin, H, Kim, B, & Lee, K 2017, 'Nanostructured materials on 3D nickel foam as electrocatalysts for water splitting' *Nanoscale*, vol. 9, no. 34, pp. 12231–12247.
- Chen, C, Khosrowabadi Kotyk, JF, & Sheehan, SW 2018, 'Progress toward Commercial Application of Electrochemical Carbon Dioxide Reduction' *Chem*, vol. 4, no. 11, pp. 2571–2586.
- Chen, CC & Song, Y 2004, 'Generalized electrolyte-NRTL model for mixed-solvent electrolyte systems'

- AIChE Journal*, vol. 50, no. 8, pp. 1928–1941.
- Cho, W 2010, *Introduction of KOGAS 's Activities on DME DME<sub>4</sub> in Stockholm, Sweden*.
- Cho, W, Song, T, Mitsos, A, McKinnon, JT, Ko, GH, Tolsma, JE, Denholm, D, & Park, T 2009, 'Optimal design and operation of a natural gas tri-reforming reactor for DME synthesis' *Catalysis Today*, vol. 139, no. 4, pp. 261–267.
- Christ, CF 1955, 'A Review of Input-Output Analysis' in *Input-Output Analysis: An Appraisal*, pp. 137–182, Princeton University Press.
- CIBO 2003, *Energy efficiency and industrial boiler efficiency - An industrial perspective*.
- City of Gold Coast 2021, *Water and sewerage pricing 2020-21*.
- Coates, GW & Moore, DR n.d., 'Discrete Metal-Based Catalysts for the Copolymerization of CO<sub>2</sub> and Epoxides: Discovery, Reactivity, Optimization, and Mechanism' *Angewandte Chemie International Edition*, vol. 43, no. 48, pp. 6618–6639.
- Collotta, M, Champagne, P, Mabee, W, & Tomasoni, G 2018, 'Wastewater and waste CO<sub>2</sub> for sustainable biofuels from microalgae' *Algal Research*, vol. 29, pp. 12–21.
- Common, MS & Salma, U 1992, 'Accounting for changes in Australian carbon dioxide emissions' *Energy Economics*, vol. 14, no. 3, pp. 217–225.
- CRI n.d., 'The Shunli CO<sub>2</sub> -to-Methanol Plant; Commercial scale production in China', Our Projects, <https://www.carbonrecycling.is/projects>.
- CRI 2017, 'Methanol Car Fleet Test Yields Positive Results', viewed 15 October 2018, <http://carbonrecycling.is/news/2017/11/1/methanol-car-fleet-test-yields-positive-results>.
- Cuéllar-Franca, RM & Azapagic, A 2015, 'Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts' *Journal of CO<sub>2</sub> Utilization*, vol. 9, pp. 82–102.
- Cuéllar Franca, RM & Azapagic, A 2017, 'Life Cycle Environmental Impacts of Carbon Capture, Storage, and Utilization' in *Encyclopedia of Sustainable Technologies*, vol. 3, pp. 447–459, Elsevier.
- Curran, MA 2012, 'Sourcing Life Cycle Inventory Data' in *Life Cycle Assessment Handbook*, pp. 105–141, John Wiley & Sons, Ltd.
- Currency Converter 2021, 'AUD USD Historical Exchange Rate', AUD USD Historical Exchange Rate, viewed 6 March 2021, <https://www.currency-converter.org.uk/currency-rates/historical/table/AUD-USD.html>.
- Daggash, HA, Patzschke, CF, Heuberger, CF, Zhu, L, Hellgardt, K, Fennell, PS, Bhawe, AN, Bardow, A, & Mac Dowell, N 2018, 'Closing the carbon cycle to maximise climate change mitigation: power-to-methanol vs. power-to-direct air capture' *Sustainable Energy Fuels*, vol. 2, no. 6, pp. 1153–1169.
- Dai, WL, Luo, SL, Yin, SF, & Au, CT 2009, 'The direct transformation of carbon dioxide to organic carbonates over heterogeneous catalysts' *Applied Catalysis A: General*, vol. 366, no. 1, pp. 2–12.
- De Luna, P, Hahn, C, Higgins, D, Jaffer, SA, Jaramillo, TF, & Sargent, EH 2019, 'What would it take for renewably powered electrosynthesis to displace petrochemical processes?' *Science (New York, N.Y.)*, vol. 364, no. 6438.
- Dechema & VCI 2009, *Position Paper on the Utilisation and Storage of CO<sub>2</sub>*.
- Delgado, A, Kjølberg, KL, & Wickson, F 2011, 'Public engagement coming of age: From theory to practice in STS encounters with nanotechnology' *Public Understanding of Science*, vol. 20, no. 6, pp. 826–845.

- Deutch, JM & Moniz, EJ 2009, *Summary for Policy Makers of the MITEI Symposium on the Retrofitting of Coal-Fired Power Plants for CO<sub>2</sub> Emissions Reductions*.
- Ding, M, Flaig, RW, Jiang, HL, & Yaghi, OM 2019, 'Carbon capture and conversion using metal-organic frameworks and MOF-based materials' *Chemical Society Reviews*, no. 10.
- Dinh, CT, Burdyny, T, Kibria, G, Seifitokaldani, A, Gabardo, CM, Pelayo García De Arquer, F, Kiani, A, Edwards, JP, De Luna, P, Bushuyev, OS, Zou, C, Quintero-Bermudez, R, Pang, Y, Sinton, D, & Sargent, EH 2018, 'CO<sub>2</sub> electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface' *Science*, vol. 360, no. 6390, pp. 783–787.
- Dioxide Materials n.d., 'Dioxide Materials has Developed Electrochemical CO<sub>2</sub> to Formate/Formic Acid 3 Compartment Cell Design with Record Performance', CO<sub>2</sub> conversion to formic acid, viewed 27 February 2021, <https://dioxidematerials.com/technology/formic-acid/>.
- Dominguez-Ramos, A, Singh, B, Zhang, X, Hertwich, EG, & Irabien, A 2015, 'Global warming footprint of the electrochemical reduction of carbon dioxide to formate' *Journal of Cleaner Production*, vol. 104, pp. 148–155.
- Dowson, G & Styring, P 2014, 'Conversion of Carbon Dioxide to Oxygenated Organics' in *Carbon Dioxide Utilisation: Closing the Carbon Cycle: First Edition*.
- Druckman, A & Jackson, T 2009, 'The carbon footprint of UK households 1990-2004: A socio-economically disaggregated, quasi-multi-regional input-output model' *Ecological Economics*, vol. 68, no. 7, pp. 2066–2077.
- Du, X, Yao, B, Gonzalez-Cortes, S, Kuznetsov, VL, Almegren, H, Xiao, T, & Edwards, PP 2015, 'Catalytic dehydrogenation of propane by carbon dioxide: A medium-temperature thermochemical process for carbon dioxide utilisation' *Faraday Discussions*, vol. 183, pp. 161–176.
- Duclos, L, Lupsea, M, Mandil, G, Svecova, L, Thivel, PX, & Laforest, V 2017, 'Environmental assessment of proton exchange membrane fuel cell platinum catalyst recycling' *Journal of Cleaner Production*, vol. 142, pp. 2618–2628.
- Dunford, NT 2012, 'Advancements in Oil and Oilseed Processing' in *Food and Industrial Bioproducts and Bioprocessing*, pp. 115–143, John Wiley & Sons, Ltd.
- Dutta, A, Farooq, S, Karimi, IA, & Khan, SA 2017, 'Assessing the potential of CO<sub>2</sub> utilization with an integrated framework for producing power and chemicals' *Journal of CO<sub>2</sub> Utilization*, vol. 19, pp. 49–57.
- Earles, JM & Halog, A 2011, 'Consequential life cycle assessment: A review' *International Journal of Life Cycle Assessment*, vol. 16, no. 5, pp. 445–453.
- EARTO 2014, *The TRL Scale as a Research & Innovation Policy Tool, EARTO Recommendations*.
- Edge Environment & Lifecycles 2016, 'Method and guidance for undertaking life cycle assessment (LCA) of bioenergy products and projects' *Report for the Australian Renewable Energy Agency (ARENA)*, no. October.
- Engelø, A, Ahmed, N, & Bureau-Cauchois, G 2014, 'Evaluation of carbon dioxide utilisation concepts: A quick and complete methodology' *Energy Procedia*, vol. 63, pp. 8010–8016.
- Environment and Climate Change Canada 2021, *National Inventory Report 1990–2019: Greenhouse Gas Sources and Sinks in Canada Canada's Submission to the United Nations Framework Convention on Climate Change*.
- European Commission 2008, 'NACE Rev. 2 – Statistical classification of economic activities in the European Community' *Office for Official Publications of the European Communities*, pp. 1–363.

- European Commission 2013, 'Recommendation 2013/179/EU on the use of common methods to measure and communicate the life cycle environmental performance of products and organisations' *Official Journal of European Union*, no. L 124, p. 210.
- European Commission - Joint Research Centre 2010, *General guide for Life Cycle Assessment - Detailed guidance International Reference Life Cycle Data System (ILCD) Handbook*.
- Evangelisti, S, Tagliaferri, C, Brett, DJL, & Lettieri, P 2017, 'Life cycle assessment of a polymer electrolyte membrane fuel cell system for passenger vehicles' *Journal of Cleaner Production*, vol. 142, pp. 4339–4355.
- Fan, G, Fujita, S, Zou, B, Nishiura, M, Meng, X, & Arai, M 2009, 'Synthesis of Diphenyl Carbonate from Phenol and Carbon Dioxide in the Presence of Carbon Tetrachloride and Zinc Chloride' *Catalysis Letters*, vol. 133, no. 3, p. 280.
- Faried, M, Samer, M, Abdelsalam, E, Yousef, RS, Attia, YA, & Ali, AS 2017, 'Biodiesel production from microalgae: Processes, technologies and recent advancements' *Renewable and Sustainable Energy Reviews*, vol. 79, pp. 893–913.
- Farrell, R & Santella, R 2019, *Australia: Biofuels Annual 2018*.
- Fernández-Dacosta, C, Stojcheva, V, & Ramirez, A 2018, 'Closing carbon cycles: Evaluating the performance of multi-product CO<sub>2</sub> utilisation and storage configurations in a refinery' *Journal of CO<sub>2</sub> Utilization*, vol. 23, no. December 2017, pp. 128–142.
- Folger, P 2018, *Carbon Capture and Sequestration (CCS) in the United States Congressional Research Service*.
- Freire-González, J 2017, 'A new way to estimate the direct and indirect rebound effect and other rebound indicators' *Energy*, vol. 128, pp. 394–402.
- 'FreSMe' n.d., viewed 15 October 2018, <http://www.fresme.eu>.
- Gadikota, G & Park, A hyung A 2014, 'Accelerated Carbonation of Ca- and Mg-Bearing Minerals and Industrial Wastes Using CO<sub>2</sub>' in *Carbon Dioxide Utilisation: Closing the Carbon Cycle: First Edition*.
- García-Gusano, D, Garraín, D, Herrera, I, Cabal, H, & Lechón, Y 2015, 'Life Cycle Assessment of applying CO<sub>2</sub> post-combustion capture to the Spanish cement production' *Journal of Cleaner Production*, vol. 104, no. 2015, pp. 328–338.
- Garnaut, R 2008, *The Garnaut Climate Change Review: Final Report*.
- Gavriilidis, A, Angeli, P, Cao, E, Yeong, KK, & Wan, YSS 2002, 'Technology and applications of microengineered reactors' *Chemical Engineering Research and Design*, vol. 80, pp. 3–30.
- Genovese, J, Harg, K, Paster, M, & Turner, JA 2009, *State-of-the-Art Hydrogen Production Cost Estimate Using Water Electrolysis: Independent Review*.
- Geoscience Australia and BREE 2014, *Australian Energy Resource Assessment - 2nd Ed.*
- Gibson, DH 1996, 'The Organometallic Chemistry of Carbon Dioxide' *Chemical Reviews*, vol. 96, no. 6, pp. 2063–2096.
- Global CCS Institute 2020, 'Global status of CCS 2020' *Global CCS Institute*, p. 40.
- Global CO<sub>2</sub> Initiative & CO<sub>2</sub> Sciences Inc. 2016, *Global Roadmap for Implementing CO<sub>2</sub> Utilization*.
- Global Industry Analysts Inc 2020, *Ethanol - Global Market Trajectory & Analytics*.
- Goetzler, W, Westphalen, D, & Burgos, J 2013, *AHRI Project 8006 – Low Global Warming Potential (GWP) Refrigerants, Phase II*.
- Google n.d., 'Manual measured area around Dalby Biorefinery', viewed 12 November 2020,

<https://www.google.com.au/maps/place/Dalby+Bio-Refinery/@-27.1467345,151.2392505,1237m/data=!3m1!1e3!4m5!3m4!1s0x6bbdf9ed5453f711:0x70725f84da5e0754!8m2!3d-27.1455431!4d151.2454315>.

- Graham, P, Hayward, J, Foster, J, & Havas, L 2020, *GenCost 2020-21: Consultation draft*.
- Grains Research and Development Corporation 2016, *Sorghum GrowNotes*.
- Grant, T, Anderson, C, & Hooper, B 2014, 'Comparative life cycle assessment of potassium carbonate and monoethanolamine solvents for CO<sub>2</sub> capture from post combustion flue gases' *International Journal of Greenhouse Gas Control*, vol. 28, pp. 35–44.
- Grant, T, Cruyppenninck, H, Eady, S, & Mata, G 2014, *AusAgLCI methodology for developing Life Cycle Inventory*.
- GreenHydrogen.dk, Siemens, DTU, & AU 2016, *HyProvide Large-Scale Alkaline Electrolyser (MW ) EUDP 11-II, 64011-0105*.
- Groom, N 2020, 'Problems plagued U.S. CO<sub>2</sub> capture project before shutdown: document' *Reuters Environment*.
- Guinée, J.B., Gorée, M, Heijungs, R, Huppes, G, Kleijn, R, de Koning, A, van Oers, L, Wegener Sleeswijk, A, Suh, S, Udo de Haes, HA, de Bruijn, H, van Duin, R, & Huijbregts, MAJ 2002, *Handbook on life cycle assessment. Operational guide to the ISO standards. I: LCA in perspective. IIa: Guide. IIb: Operational annex. III: Scientific background*, Kluwer Academic Publishers, Dordrecht.
- Guinée, Jeroen B, Heijungs, R, Huppes, G, Zamagni, A, Masoni, P, Buonamici, R, Ekvall, T, & Rydberg, T 2011, 'Life Cycle Assessment: Past, Present, and Future' *Environmental Science & Technology*, vol. 45, no. 1, pp. 90–96.
- Gupta, N, Gattrell, M, & MacDougall, B 2006, 'Calculation for the cathode surface concentrations in the electrochemical reduction of CO<sub>2</sub> in KHCO<sub>3</sub> solutions' *Journal of Applied Electrochemistry*, vol. 36, no. 2, pp. 161–172.
- Gutiérrez-Martín, F, Ochoa-Mendoza, A, & Rodríguez-Antón, LM 2015, 'Pre-investigation of water electrolysis for flexible energy storage at large scales: The case of the Spanish power system' *International Journal of Hydrogen Energy*, vol. 40, no. 15, pp. 5544–5551.
- Haas, T, Krause, R, Weber, R, Demler, M, & Schmid, G 2018, 'Technical photosynthesis involving CO<sub>2</sub> electrolysis and fermentation' *Nature Catalysis*, vol. 1, no. 1, pp. 32–39.
- Hall, PJ, Wilson, IAG, & Rennie, A 2015, 'CO<sub>2</sub>-Derived Fuels for Energy Storage' in P. Styring, E. A. Quadrelli, & K. Armstrong (eds.), *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, 1st edn, pp. 33–44, Elsevier.
- Hanak, DP & Manovic, V 2016, 'Calcium looping with supercritical CO<sub>2</sub> cycle for decarbonisation of coal-fired power plant' *Energy*, vol. 102, pp. 343–353.
- Harkin, T 2012, *Multi-Objective Optimisation of CCS using simulation, heat integration and cost estimation*, doctoral thesis, Monash University.
- Harned, HS & Davis, R 1943, 'The Ionization Constant of Carbonic Acid in Water and the Solubility of Carbon Dioxide in Water and Aqueous Salt Solutions from 0 to 50°' *Journal of the American Chemical Society*, vol. 65, no. 10, pp. 2030–2037.
- Harned, HS & Scholes, SR 1941, 'The Ionization Constant of HCO<sub>3</sub><sup>-</sup> from 0 to 50°' *Journal of the American Chemical Society*, vol. 63, no. 6, pp. 1706–1709.
- Hasan, MMF, First, EL, Boukouvala, F, & Floudas, CA 2015, 'A multi-scale framework for CO<sub>2</sub> capture, utilization, and sequestration: CCUS and CCU' *Computers and Chemical Engineering*, vol. 81, pp.



- Héder, M 2017, 'From NASA to EU: the evolution of the TRL scale in Public Sector Innovation' *The Innovation Journal*, vol. 22, no. 3, pp. 1–23.
- Heijungs, R & Guinée, J 2012, 'An Overview of the Life Cycle Assessment Method - Past, Present, and Future' in *Life Cycle Assessment Handbook: A Guide for Environmentally Sustainable Products*, pp. 15–41.
- Hellweg, S & Canals, LMI 2014, 'Emerging approaches, challenges and opportunities in life cycle assessment' *Science*, vol. 344, no. 6188, pp. 1109–1113.
- Hertwich, E & Katzmayer, M 2003, *Examples of Sustainable Consumption: Review, Classification and Analysis Final Report to Mitsubishi Research Inc. and the Society for Non-Traditional Technology, Japan*.
- Hertwich, EG 2005, 'Consumption and the Rebound Effect - An Industrial Ecology Perspective' *Journal of Industrial Ecology*, vol. 9, no. 1, pp. 85 – 98.
- Hertwich, EG & Peters, GP 2009, 'Carbon footprint of nations: A global, trade-linked analysis' *Environmental Science and Technology*, vol. 43, no. 16, pp. 6414–6420.
- Herzog, H, Drake, E, & Adams, E 1997, *CO<sub>2</sub> Capture Reuse and Storage Technologies for Mitigating Global Climate Change*.
- Heuze, V, Tran, G, Giger-Reverdin, S, Bastianelli, D, & Lebas, F 2015, 'Sorghum by-products', Feedipedia, a programme by INRAE, CIRAD, AFZ and FAO, viewed 19 November 2020, <https://www.feedipedia.org/node/752>.
- Heuze, V, Tran, G, Hassoun, P, Bastianelli, D, & Lebas, F 2019, 'Cottonseed meal', Feedipedia, a programme by INRAE, CIRAD, AFZ and FAO.
- Heuze, V, Tran, G, & Kaushik, S 2020, 'Soybean meal', Feedipedia, a programme by INRAE, CIRAD, AFZ and FAO, viewed 19 February 2021, <https://www.feedipedia.org/node/674>.
- Ho, MT, Allinson, GW, & Wiley, DE 2008, 'Reducing the Cost of CO<sub>2</sub> Capture from Flue Gases Using Pressure Swing Adsorption' *Industrial & Engineering Chemistry Research*, vol. 47, no. 14, pp. 4883–4890.
- Holmes, G & Keith, DW 2012, 'An air-liquid contactor for large-scale capture of CO<sub>2</sub> from air' *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 370, no. 1974, pp. 4380–4403.
- Hoppe, W, Thonemann, N, & Bringezu, S 2018, 'Life Cycle Assessment of Carbon Dioxide-Based Production of Methane and Methanol and Derived Polymers' *Journal of Industrial Ecology*, vol. 22, no. 2, pp. 327–340.
- Hori, Y 2008, 'Electrochemical CO<sub>2</sub> Reduction on Metal Electrodes' in C. G. Vayenas, R. E. White, & M. E. Gamboa-Aldeco (eds.), *Modern Aspects of Electrochemistry*, pp. 89–189, Springer New York, New York.
- Huang, CH & Tan, CS 2014, 'A review: CO<sub>2</sub> utilization' *Aerosol and Air Quality Research*, vol. 14, no. 2, pp. 480–499.
- Hudkins, JR, Wheeler, DG, Peña, B, & Berlinguette, CP 2016, 'Rapid prototyping of electrolyzer flow field plates' *Energy and Environmental Science*, vol. 9, no. 11, pp. 3417–3423.
- Huijbregts, MA., Steinmann, ZJNN, Elshout, PMFMF, Stam, G, Verones, F, Vieira, MDMD., Zijp, M, & van Zelm, R 2016, 'ReCiPe 2016: A harmonized life cycle impact assessment method at midpoint and endpoint level - Report 1: characterization' *National Institute for Public Health and the*

- Huijbregts, MAJ 1998, 'Application of uncertainty and variability in LCA. Part I: A general framework for the analysis of uncertainty and variability in life cycle assessment' *International Journal of Life Cycle Assessment*, vol. 3, no. 5, pp. 273–280.
- Huijbregts, MAJ, Gilijamse, W, Ragas, AMJ, & Reijnders, L 2003, 'Evaluating Uncertainty in Environmental Life-Cycle Assessment. A Case Study Comparing Two Insulation Options for a Dutch One-Family Dwelling' *Environmental Science & Technology*, vol. 37, no. 11, pp. 2600–2608.
- Hung, C-J, Liu, C-H, Wang, C-H, Chen, W-H, Shen, C-W, Liang, H-C, & Ko, T-H 2015, 'Effect of conductive carbon material content and structure in carbon fiber paper made from carbon felt on the performance of a proton exchange membrane fuel cell' *Renewable Energy*, vol. 78, pp. 364–373.
- Iaquaniello, G, Centi, G, Salladini, A, Palo, E, Perathoner, S, & Spadaccini, L 2017, 'Waste-to-methanol: Process and economics assessment' *Bioresource Technology*, vol. 243, pp. 611–619.
- IEA 2017, *Energy Technology Perspectives 2017. Catalysing Energy Technology Transformations*, doi:/10.1787/energy\_tech-2017-en.
- IEA 2019a, *Putting CO2 to Use*.
- IEA 2019b, *The Future of Hydrogen The Future of Hydrogen*, OECD, doi:/10.1787/1e0514c4-en.
- IEA 2020a, 'Annual ethylene capacity/demand growth and regional price developments, 2015–2020', viewed 15 February 2021, <https://www.iea.org/data-and-statistics/charts/annual-ethylene-capacity-demand-growth-and-regional-price-developments-2015-2020>.
- IEA 2020b, *CCUS in Power*.
- IEA 2020c, *CO2 Emissions from Fuel Combustion CO2 Emissions from fuel combustion dataset*.
- IEA 2020d, *Energy Technology Perspectives 2020 Special Report on Carbon Capture Utilisation and Storage*.
- IEAGHG 2018, *Greenhouse Gas Emissions Accounting for CO2 Capture and Utilisation (CCU) Technologies - Synthesis of Research Findings*.
- Igos, E, Benetto, E, Meyer, R, Baustert, P, & Othoniel, B 2019, 'How to treat uncertainties in life cycle assessment studies?' *International Journal of Life Cycle Assessment*, vol. 24, pp. 794–807.
- IHS Markit 2020, 'Ethylene: Chemical Economics Handbook', Chemical Economics Handbook.
- Ikushima, Y, Saito, N, Arai, M, & Arai, K 1991, 'Solvent Polarity Parameters of Supercritical Carbon Dioxide as Measured by Infrared Spectroscopy' *Bulletin of the Chemical Society of Japan*, vol. 64, no. 7, pp. 2224–2229.
- International Standards Organisation (ISO) 'ISO 14040: Environmental Management - Life Cycle Assessment - Principles and Framework', (2006).
- International Standards Organisation (ISO) 'ISO 14044: Environmental Management - Life Cycle Assessment - Requirements and Guidelines', (2006).
- IPCC 1990, *IPCC First assessment report* eds. J. T. Houghton, G. J. Jenkins, & J. J. Ephraums, World Meteorological Organization, doi:/10.1097/MOP.0b013e3283444c89.
- IPCC 1996, *Climate Change 1995. The Science of Climate Change Contribution of WGI to the Second Assessment Report of the Intergovernmental Panel on Climate Change*, doi:/10.1017/CBO9781107415324.004.
- IPCC 2005, *IPCC Special Report on Carbon Dioxide Capture and Storage Working Group III of the Intergovernmental Panel on Climate Change*, doi:/10.1002/anie.201000431.

- IPCC 2006, *2006 IPCC Guidelines for national greenhouse gas inventories* eds. H. S. Eggleston, L. Buendia, K. Miwa, T. Ngara, & K. Tanabe, *Prepared by the National Greenhouse Gas Inventories Program*, Geneva, Switzerland.
- IPCC 2018, *Summary For Policymakers* ed. and T. W. Masson-Delmotte, V., P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P.R. Shukla, A. Pirani, W. Moufouma-Okia, C. Péan, R. Pidcock, S. Connors, J.B.R. Matthews, Y. Chen, X. Zhou, M.I. Gomis, E. Lonnoy, T. Maycock, M. Tignor, *Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change*, World Meteorological Organization, Geneva, Switzerland.
- IRENA 2020, *Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.5°C Climate Goal*.
- Isaksen, I, Ramaswamy, V, Rodhe, H, & Wighley, T 2002, *Climate Change 1992: The supplementary report to the IPCC scientific assessment. Section A2. Radiative forcing of climate change Climate Change 1992: The supplementary report to the IPCC scientific assessment*, vol. 57, doi:/10.1256/004316502320517362.
- Ishaq, H, Siddiqui, O, Chehade, G, & Dincer, I 2021, 'A solar and wind driven energy system for hydrogen and urea production with CO<sub>2</sub> capturing' *International Journal of Hydrogen Energy*, vol. 46, no. 6, pp. 4749–4760.
- Izumi, Y 1997, 'Selective ethanol synthesis from carbon dioxide' *Platinum Metals Review*, vol. 41, no. 4, pp. 166–170.
- Jadhav, SG, Vaidya, PD, Bhanage, BM, & Joshi, JB 2014, 'Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies' *Chemical Engineering Research and Design*, vol. 92, no. 11, pp. 2557–2567.
- Jambo, SA, Abdulla, R, Mohd Azhar, SH, Marbawi, H, Gansau, JA, & Ravindra, P 2016, 'A review on third generation bioethanol feedstock' *Renewable and Sustainable Energy Reviews*, vol. 65, pp. 756–769.
- James, DE 1980, 'A System of Energy Accounts for Australia' *Economic Record*, vol. 56, no. 153, pp. 171–181.
- Jang, JG, Kim, GM, Kim, HJ, & Lee, HK 2016, 'Review on recent advances in CO<sub>2</sub>utilization and sequestration technologies in cement-based materials' *Construction and Building Materials*, vol. 127.
- Jessop, PG, Mercer, SM, & Heldebrant, DJ 2012, 'CO<sub>2</sub>-triggered switchable solvents, surfactants, and other materials' *Energy & Environmental Science*, vol. 5, no. 6, p. 7240.
- Jessop, PG & Subramaniam, B 2007, 'Gas-Expanded Liquids' *Chemical Reviews*, vol. 107, no. 6, pp. 2666–2694.
- Jia, M, Fan, Q, Liu, S, Qiu, J, & Sun, Z 2019, 'Single-atom catalysis for electrochemical CO<sub>2</sub> reduction' *Current Opinion in Green and Sustainable Chemistry*, vol. 16, pp. 1–6.
- Jonasson, K & Sanden, B 2004, 'Time and Scale Aspects in Life Cycle Assessment of Emerging Technologies' *Environmental Systems Analysis (ESA)*, p. 52.
- Jones, CR 2015, 'Chapter 15 - Understanding and Assessing Public Perceptions of Carbon Dioxide Utilisation (CDU) Technologies' in P. Styring, E. A. Quadrelli, & K. Armstrong (eds.), *Carbon Dioxide Utilisation*, pp. 273–283, Elsevier, Amsterdam.
- Jones, CR, Radford, RL, Armstrong, K, & Styring, P 2014, 'What a waste! Assessing public perceptions of Carbon Dioxide Utilisation technology' *Journal of CO<sub>2</sub> Utilization*, vol. 7, pp. 51–54.

- Joos, F, Roth, R, Fuglestvedt, JS, Peters, GP, Enting, IG, Von Bloh, W, Brovkin, V, Burke, EJ, Eby, M, Edwards, NR, Friedrich, T, Frölicher, TL, Halloran, PR, Holden, PB, Jones, C, Kleinen, T, Mackenzie, FT, Matsumoto, K, Meinshausen, M, Plattner, GK, Reisinger, A, Segschneider, J, Shaffer, G, Steinacher, M, Strassmann, K, Tanaka, K, Timmermann, A, & Weaver, AJ 2013, 'Carbon dioxide and climate impulse response functions for the computation of greenhouse gas metrics: A multi-model analysis' *Atmospheric Chemistry and Physics*, vol. 13, no. 5, pp. 2793–2825.
- Jouny, M, Luc, W, & Jiao, F 2018, 'General Techno-Economic Analysis of CO<sub>2</sub> Electrolysis Systems' *Industrial and Engineering Chemistry Research*, vol. 57, no. 6, pp. 2165–2177.
- Karamad, M, Tripkovic, V, & Rossmeisl, J 2014, 'Intermetallic alloys as CO electroreduction catalysts—role of isolated active sites' *ACS Catalysis*, vol. 4, no. 7, pp. 2268–2273.
- Keith, DW, Holmes, G, St. Angelo, D, & Heidel, K 2018, 'A Process for Capturing CO<sub>2</sub> from the Atmosphere' *Joule*, vol. 2, no. 8, pp. 1573–1594.
- Khalilpour, KR & Zafaranloo, A 2020, 'Generic techno-economic optimization methodology for concurrent design and operation of solvent-based PCC processes' *International Journal of Greenhouse Gas Control*, vol. 99, no. June, p. 103079.
- Khalilpour, R 2014, 'Flexible operation scheduling of a power plant integrated with PCC processes under market dynamics' *Industrial and Engineering Chemistry Research*, vol. 53, no. 19, pp. 8132–8146.
- Khalilpour, R & Abbas, A 2011, 'HEN optimization for efficient retrofitting of coal-fired power plants with post-combustion carbon capture' *International Journal of Greenhouse Gas Control*, vol. 5, no. 2, pp. 189–199.
- Khan, C, Amin, R, & Madden, G 2013, 'Carbon dioxide injection for enhanced gas recovery and storage (reservoir simulation)' *Egyptian Journal of Petroleum*, vol. 22, no. 2, pp. 225–240.
- Klankermayer, J & Leitner, W 2016, 'Harnessing renewable energy with CO<sub>2</sub> for the chemical value chain: challenges and opportunities for catalysis' *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 374, no. 2061, p. 20150315.
- Klinger Australia n.d., 'Klinger SOFT-CHEM', viewed 22 November 2020, <https://www.klinger.com.au/products/ptfe-gasket-materials/klinger-soft-chem>.
- Klöpffer, W 2006, 'The role of SETAC in the development of LCA' *International Journal of Life Cycle Assessment*, vol. 11, pp. 116–122.
- Koj, JC, Schreiber, A, Zapp, P, & Marcuello, P 2015, *Life Cycle Assessment of Improved High Pressure Alkaline Electrolysis STE Research Report*, vol. 75.
- Kondaveeti, S, Abu-Reesh, IM, Mohanakrishna, G, Bulut, M, & Pant, D 2020, 'Advanced Routes of Biological and Bio-electrocatalytic Carbon Dioxide (CO<sub>2</sub>) Mitigation Toward Carbon Neutrality' *Frontiers in Energy Research*, vol. 8, p. 94.
- Kondratenko, E V, Mul, G, Baltrusaitis, J, Larrazábal, GO, & Pérez-Ramírez, J 2013, 'Status and perspectives of CO<sub>2</sub> conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes' *Energy Environ. Sci.*, vol. 6, no. 11, pp. 3112–3135.
- Kowalewski, J 2009, 'Methodology of the Input-Output Analysis' *HWI Research Papers*, pp. 1–25.
- Kramer, D 2018, 'Can carbon capture from air shift the climate change equation?' *Physics Today*, vol. 71, no. 9, pp. 26–29.
- Kuhl, KP, Cave, ER, Abram, DN, & Jaramillo, TF 2012, 'New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces' *Energy and Environmental Science*, vol. 5, no. 5, pp. 7050–7059.

- Kusama, H, Okabe, K, Sayama, K, & Arakawa, H 1996, 'CO<sub>2</sub> hydrogenation to ethanol over promoted Rh/SiO<sub>2</sub> catalysts' *Catalysis Today*.
- Landgraf, M 2019, August, 'Carbon-neutral Fuels from Air and Green Power' *KIT Press Release*, p. 4.
- Langanke, J, Wolf, A, & Peters, M 2015, 'Polymers from CO<sub>2</sub>-An Industrial Perspective' in P. Styring, E. A. Quadrelli, & K. Armstrong (eds.), *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, 1st edn, Elsevier, Amsterdam.
- LanzaTech 2017, 'LanzaTech processes', viewed 20 November 2018, [https://www.energy.gov/sites/prod/files/2017/07/f35/BETO\\_2017WTE-Workshop\\_SeanSimpson-LanzaTech.pdf](https://www.energy.gov/sites/prod/files/2017/07/f35/BETO_2017WTE-Workshop_SeanSimpson-LanzaTech.pdf).
- Lekve Bjelle, E, Steen-Olsen, K, & Wood, R 2018, 'Climate change mitigation potential of Norwegian households and the rebound effect' *Journal of Cleaner Production*, vol. 172, pp. 208–217.
- Lenzen, M 1998, 'Primary energy and greenhouse gases embodied in Australian final consumption: an input-output analysis' *Energy Policy*, vol. 26, no. 6, pp. 495–506.
- Leontief, W 1970, 'Environmental Repercussions and the Economic Structure: An Input-Output Approach' *The Review of Economics and Statistics*.
- Leontief, WW 1936, 'Quantitative Input and Output Relations in the Economic Systems of the United States' *The Review of Economics and Statistics*, vol. 18, no. 3, p. 105.
- Leonzio, G 2018, 'State of art and perspectives about the production of methanol, dimethyl ether and syngas by carbon dioxide hydrogenation' *Journal of CO<sub>2</sub> Utilization*, vol. 27, no. July, pp. 326–354.
- Li, F, Li, YC, Wang, Z, Li, J, Nam, DH, Lum, Y, Luo, M, Wang, X, Ozden, A, Hung, SF, Chen, B, Wang, Y, Wicks, J, Xu, Y, Li, Y, Gabardo, CM, Dinh, CT, Wang, Y, Zhuang, TT, Sinton, D, & Sargent, EH 2020, 'Cooperative CO<sub>2</sub>-to-ethanol conversion via enriched intermediates at molecule-metal catalyst interfaces' *Nature Catalysis*, vol. 3, no. 1, pp. 75–82.
- Li, H & Oloman, C 2005, 'The electro-reduction of carbon dioxide in a continuous reactor' *Journal of Applied Electrochemistry*, vol. 35, no. 10, pp. 955–965.
- Li, H & Oloman, C 2006, 'Development of a continuous reactor for the electro-reduction of carbon dioxide to formate - Part 1: Process variables' *Journal of Applied Electrochemistry*, vol. 36, no. 10, pp. 1105–1115.
- Li, H & Oloman, C 2007, 'Development of a continuous reactor for the electro-reduction of carbon dioxide to formate - Part 2: Scale-up' *Journal of Applied Electrochemistry*, vol. 37, no. 10, pp. 1107–1117.
- Li, Z, Sharma, M, Khalilpour, R, & Abbas, A 2013, 'Optimal operation of solvent-based post-combustion carbon capture processes with reduced models' *Energy Procedia*, vol. 37, pp. 1500–1508.
- Liang, Y, Liu, Q, Asiri, AM, Sun, X, & He, Y 2015, 'Nickel-iron foam as a three-dimensional robust oxygen evolution electrode with high activity' *International Journal of Hydrogen Energy*, vol. 40, no. 39, pp. 13258–13263.
- Licence, P, Ke, J, Sokolova, M, Ross, SK, & Poliakov, M 2003, 'Chemical reactions in supercritical carbon dioxide: From laboratory to commercial plant' *Green Chemistry*, vol. 5, no. 2, pp. 99–104.
- Lifset, R 2009, 'Industrial Ecology in the Age of Input-Output Analysis' in S. Suh (ed.), *Handbook of Input-Output Economics in Industrial Ecology*, pp. 3–21, Springer Netherlands.
- Lim, RJ, Xie, M, Sk, MA, Lee, J-M, Fisher, A, Wang, X, & Lim, KH 2014, 'A review on the electrochemical reduction of CO<sub>2</sub> in fuel cells, metal electrodes and molecular catalysts' *Catalysis Today*, vol. 233, pp. 169–180.
- Liu, CM, Sandhu, NK, McCoy, ST, & Bergerson, JA 2020, 'A life cycle assessment of greenhouse gas

- emissions from direct air capture and Fischer-Tropsch fuel production' *Sustainable Energy and Fuels*, vol. 4, no. 6, pp. 3129–3142.
- Liu, PS & Liang, KM 2000, 'Preparation and corresponding structure of nickel foam' *Materials Science and Technology*, vol. 16, no. 5, pp. 575–578.
- Liu, W, Du, K, Liu, L, Zhang, J, Zhu, Z, Shao, Y, & Li, M 2017, 'One-step electroreductively deposited iron-cobalt composite films as efficient bifunctional electrocatalysts for overall water splitting' *Nano Energy*, vol. 38, no. November 2016, pp. 576–584.
- Liu, Y, Wang, ZU, & Zhou, H-C 2012, 'Recent advances in carbon dioxide capture with metal-organic frameworks' *Greenhouse Gases: Science and Technology*, vol. 2, no. 4, pp. 239–259.
- Lixon, B, Thomassin, PJ, & Hamaide, B 2008, 'Industrial output restriction and the Kyoto protocol: An input-output approach with application to Canada' *Ecological Economics*, vol. 68, no. 1–2, pp. 249–258.
- Löhne, A & Weißing, B 2017, 'The vector linear program solver Bensolve - notes on theoretical background' *European Journal of Operational Research*, vol. 260, no. 3, pp. 807–813.
- Luu, MT, Milani, D, Bahadori, A, & Abbas, A 2015, 'A comparative study of CO<sub>2</sub> utilization in methanol synthesis with various syngas production technologies' *Journal of CO<sub>2</sub> Utilization*, vol. 12, pp. 62–76.
- Ma, M, Clark, EL, Therkildsen, KT, Dalsgaard, S, Chorkendorff, I, & Seger, B 2020, 'Insights into the carbon balance for CO<sub>2</sub> electroreduction on Cu using gas diffusion electrode reactor designs' *Energy and Environmental Science*, vol. 13, no. 3, pp. 977–985.
- Ma, T, Fan, Q, Li, X, Qiu, J, Wu, T, & Sun, Z 2019, 'Graphene-based materials for electrochemical CO<sub>2</sub> reduction' *Journal of CO<sub>2</sub> Utilization*, vol. 30, no. February, pp. 168–182.
- Majeau-Bettez, G, Hawkins, TR, & Strømman, AH 2011, 'Life Cycle Environmental Assessment of Lithium-Ion and Nickel Metal Hydride Batteries for Plug-In Hybrid and Battery Electric Vehicles' *Environmental Science & Technology*, vol. 45, no. 10, pp. 4548–4554.
- Malik, K, Singh, S, Basu, S, & Verma, A 2017, 'Electrochemical reduction of CO<sub>2</sub> for synthesis of green fuel' *Wiley Interdisciplinary Reviews: Energy and Environment*, vol. 6, no. 4, p. 244.
- Mantra Venture Group Ltd 2014, 'Mantra Officially Launches Pilot Plant Project', viewed 20 August 2018, <https://www.globenewswire.com/news-release/2014/03/25/1395013/0/en/Mantra-Officially-Launches-Pilot-Plant-Project.html>.
- Maring, BJ & Webley, PA 2013, 'A new simplified pressure/vacuum swing adsorption model for rapid adsorbent screening for CO<sub>2</sub> capture applications' *International Journal of Greenhouse Gas Control*, vol. 15, pp. 16–31.
- Markewitz, P, Kuckshinrichs, W, Leitner, W, Linssen, J, Zapp, P, Bongartz, R, Schreiber, A, & Müller, TE 2012, 'Worldwide innovations in the development of carbon capture technologies and the utilization of CO<sub>2</sub>' *Energy and Environmental Science*, vol. 5, no. 6, pp. 7281–7305.
- Marriott, R, Jessop, P, & Barnes, M 2015, 'CO<sub>2</sub>-based Solvents' in P. Styring, E. A. Quadrelli, & K. Armstrong (eds.), *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, 1st edn, Elsevier, Amsterdam.
- Martín, M & Grossmann, IE 2017, 'Towards zero CO<sub>2</sub> emissions in the production of methanol from switchgrass. CO<sub>2</sub> to methanol' *Computers and Chemical Engineering*, vol. 105, pp. 308–316.
- Masel, R, Ni, R, Liu, Z, Chen, Q, Kutz, R, Nereng, L, Lutz, D, & Lewinski, K 2014, 'Unlocking the potential of CO<sub>2</sub> conversion to fuels and chemicals as an economically viable route to CCR' *Energy*

- Procedia*, vol. 63, pp. 7959–7962.
- Maxwell, GR 2012, ‘Synthetic nitrogen products’ in *Handbook of Industrial Chemistry and Biotechnology: Twelfth Edition*.
- Mazzotti, M, Baciocchi, R, Desmond, MJ, & Socolow, RH 2013, ‘Direct air capture of CO<sub>2</sub> with chemicals: Optimization of a two-loop hydroxide carbonate system using a countercurrent air-liquid contactor’ *Climatic Change*, vol. 118, no. 1, pp. 119–135.
- ‘MefCO<sub>2</sub>’ n.d., viewed 15 October 2018, <http://www.mefco2.eu/mefco2.php>.
- Metz, B, Davidson, O, de Coninck, H, Loos, M, & Meyer, L 2005, *IPCC Special Report on Carbon Dioxide Capture and Storage Intergovernmental Panel on Climate Change*, doi:/10.1002/anie.201000431.
- MicroLab Scientific n.d., ‘Hydrophobic PTFE Membrane Filter’, viewed 12 April 2021, <http://www.microlabscientific.com/Hydrophobic-PTFE-Membrane-Filter.html>.
- Miller, RE & Blair, PD 2009, *Input–Output Analysis: Foundations and Extensions*, Second Edi, Cambridge University Press, Cambridge.
- Millero, FJ 1995, ‘Thermodynamics of the carbon dioxide system in the oceans’ *Geochimica et Cosmochimica Acta*, vol. 59, no. 4, pp. 661–677.
- Ministry of Internal Affairs and Communications 2009, *Coefficients for Input-Output Analysis and Computation Methods. Chapter IV*, vol. 2005 Input.
- MIT 2016, *Boundary Dam Fact Sheet: Carbon Dioxide Capture and Storage Project*.
- Mitsui Chemicals n.d., ‘CCU (Carbon Capture Usage) Technologies’, Environmental Protection, viewed 20 November 2018, <https://jp.mitsuicheicals.com/en/sustainability/rc/environment/ghg.htm>.
- Mitsui Chemicals 2008, *Mitsui Chemicals to Establish a Pilot Facility to Study a Methanol Synthesis Process from CO<sub>2</sub>*.
- Mohd Nawi, WNR, Wan Alwi, SR, Manan, ZA, & Klemesš, JJ 2016, ‘Pinch Analysis targeting for CO<sub>2</sub> Total Site planning’ *Clean Technologies and Environmental Policy*, vol. 18, no. 7, pp. 2227–2240.
- Mollerup, J 1975, ‘Vapour/liquid equilibrium in ethylene + carbon dioxide and ethane + carbon dioxide’ *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, vol. 71, p. 2351.
- Moravvej, Z, Makarem, MA, & Rahimpour, MR 2019, ‘Chapter 20 - The fourth generation of biofuel’ in A. Basile & F. Dalena (eds.), *Second and Third Generation of Feedstocks*, pp. 557–597, Elsevier.
- Moyler, DA 1993, ‘Extraction of essential oils with carbon dioxide’ *Flavour and Fragrance Journal*, vol. 8, no. 5, pp. 235–247.
- Müller, K & Arlt, W 2014, ‘Shortcut evaluation of chemical carbon dioxide utilization processes’ *Chemical Engineering and Technology*, vol. 37, no. 9, pp. 1612–1615.
- Müller, LJ, Kätelhön, A, Bringezu, S, McCoy, S, Suh, S, Edwards, R, Sick, V, Kaiser, S, Cuéllar-Franca, R, El Khamlichi, A, Lee, JH, Von Der Assen, N, & Bardow, A 2020, ‘The carbon footprint of the carbon feedstock CO<sub>2</sub>’ *Energy and Environmental Science*, vol. 13, no. 9, pp. 2979–2992.
- Muradov, N 2014, ‘Industrial Utilization of CO<sub>2</sub>: A Win–Win Solution’ in *Liberating Energy from Carbon: Introduction to Decarbonization*, pp. 325–383, Springer New York, New York, NY.
- Myers, AL & Prausnitz, JM 1965, ‘Thermodynamics of mixed-gas adsorption’ *AIChE Journal*, vol. 11, no. 1, pp. 121–127.
- Myers, DJ, Wang, X, Kariuki, N, DeCrane, S, Nowicki, T, Arisetty, S, Subbaraman, R, Ahluwalia, R, Gilbert, JA, Puchala, B, Holby, E, Morgan, D, Ball, SC, Sharman, J, Theobald, B, Hards, GA,

- Gummalla, M, Z. Yang, S, & Han, B 2012, *Polymer Electrolyte Fuel Cell Lifetime Limitations: The Role of Electrocatalyst Degradation ECS Meeting Abstracts*, doi:/10.1149/MA2012-02/13/1276.
- Myhre, G, Shindell, D, Bréon, F-M, Collins, W, Fuglestad, J, Huang, J, Koch, D, Lamarque, J-F, Lee, D, Mendoza, B, Nakajima, T, Robock, A, Stephens, G, Takemura, T, & Zhang, H 2013, *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Chapter 8. Anthropogenic and Natural Radiative Forcing Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, doi:/10.1017/CBO9781107415324.018.
- Nabil, S, McCoy, S, & Kibria, MG 2021, 'Comparative life cycle assessment of electrochemical upgrading of CO<sub>2</sub> to fuels and feedstocks' *Green Chemistry*, vol. 23, no. 2, pp. 867–880.
- Narinesingh, J & Alexander, D 2014, 'CO<sub>2</sub> Enhanced gas recovery and geologic sequestration in condensate reservoir: A simulation study of the effects of injection pressure on condensate recovery from reservoir and CO<sub>2</sub> storage efficiency' *Energy Procedia*, vol. 63, pp. 3107–3115.
- 'New Sky Energy' n.d., viewed 19 October 2018, <http://www.newskyenergy.com/carboncycle/>.
- Nguyen, HT, Aviso, KB, Le, DQ, Kojima, N, & Tokai, A 2018, 'A linear programming input–output model for mapping low-carbon scenarios for Vietnam in 2030' *Sustainable Production and Consumption*, vol. 16, pp. 134–140.
- Nieskens, DLS, Ferrari, D, Liu, Y, & Kolonko, R 2011, 'The conversion of carbon dioxide and hydrogen into methanol and higher alcohols' *Catalysis Communications*, vol. 14, no. 1, pp. 111–113.
- Noack, C, Burggraf, F, Hosseiny, SS, Lettenmeier, P, Kolb, S, Belz, S, Kallo, J, Friedrich, KA, Pregger, T, Cao, K-K, Heide, D, Naegler, T, Borggreffe, F, Bünger, U, Michalski, J, Raksha, T, Voglstätter, C, Smolinka, T, Crotogino, F, Donadei, S, Horvath, P-L, & Schneider, G-S 2015, *Studie über die Planung einer Demonstrationsanlage zur Wasserstoff-Kraftstoffgewinnung durch Elektrolyse mit Zwischenspeicherung in Salzkavernen unter Druck*.
- North, M 2015, 'What is CO<sub>2</sub>? Thermodynamics, Basic Reactions and Physical Chemistry' in P. Styring, E. A. Quadrelli, & K. Armstrong (eds.), *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, 1st edn, Elsevier, Amsterdam.
- Novick, D 1959, *The Federal Budget as an Indicator of Government Intentions and the Implications of Intentions*, RAND Corporation.
- 'Novomer' n.d., viewed 18 October 2018, <https://www.novomer.com>.
- OECD/FAO 2019, 'OECD-FAO Agricultural Outlook 2019-2028', p. 326, OECD Publishing, Paris/FAO, Rome.
- Oexmann, J, Kather, A, Linnenberg, S, & Liebenthal, U 2012, 'Review: Post-combustion CO<sub>2</sub> capture: chemical absorption processes in coal-fired steam power plants' *Greenhouse Gases: Science and Technology*, vol. 2, pp. 80–98.
- Olah, GA 2013, 'Towards oil independence through renewable methanol chemistry' *Angewandte Chemie - International Edition*, vol. 52, no. 1, pp. 104–107.
- Olah, GA, Goepfert, A, & Prakash, GKS 2009a, *Beyond Oil and Gas: The Methanol Economy: Second Edition Beyond Oil and Gas: The Methanol Economy: Second Edition*.
- Olah, GA, Goepfert, A, & Prakash, GKS 2009b, 'Chemical Recycling of Carbon Dioxide to Methanol and Dimethyl Ether : From Greenhouse Gas to Renewable , Environmentally Carbon Neutral Fuels and Synthetic Hydrocarbons' *Journal of Organic Chemistry*, vol. 74, no. 2, 2009, pp. 487–498.



- Oloman, C & Li, H 2008, 'Electrochemical Processing of Carbon Dioxide' *ChemSusChem*, vol. 1, no. 5, pp. 385–391.
- Omae, I 2012, 'Recent developments in carbon dioxide utilization for the production of organic chemicals' *Coordination Chemistry Reviews*, vol. 256, no. 13–14, pp. 1384–1405.
- Ondrey, G 2020, June 16, 'Dow and Shell team up to develop electric-cracking technology' *Chemical Engineering*.
- Osman, AI, Hefny, M, Abdel Maksoud, MIA, Elgarahy, AM, & Rooney, DW 2021, 'Recent advances in carbon capture storage and utilisation technologies: a review' *Environmental Chemistry Letters*, vol. 19, no. 2, pp. 797–849.
- Otto, A, Grube, T, Schiebahn, S, & Stolten, D 2015, 'Closing the loop: Captured CO<sub>2</sub> as a feedstock in the chemical industry' *Energy and Environmental Science*, vol. 8, no. 11, pp. 3283–3297.
- Palacios-Bereche, R, Ensinas, A V, Modesto, M, & Nebra, SA 2015, 'Double-effect distillation and thermal integration applied to the ethanol production process' *Energy*, vol. 82, pp. 512–523.
- Pan, ZF, An, L, Zhao, TS, & Tang, ZK 2018, 'Advances and challenges in alkaline anion exchange membrane fuel cells' *Progress in Energy and Combustion Science*, vol. 66, pp. 141–175.
- Park, S, Lee, J-W, & Popov, BN 2008, 'Effect of PTFE content in microporous layer on water management in PEM fuel cells' *Journal of Power Sources*, vol. 177, no. 2, pp. 457–463.
- Pascual-González, J, Jiménez-Esteller, L, Guillén-Gosálbez, G, Siirola, JJ, & Grossmann, IE 2016, 'Macro-economic multi-objective input-output model for minimizing CO<sub>2</sub> emissions: Application to the U.S. economy' *AIChE Journal*, vol. 62, no. 10, pp. 3639–3656.
- Patil, YP, Tambade, PJ, Jagtap, SR, & Bhanage, BM 2010, 'Carbon dioxide: A renewable feedstock for the synthesis of fine and bulk chemicals' *Frontiers of Chemical Engineering in China*, no. 4, pp. 213–235.
- Pekdemir, T 2015, 'Chapter 14 - Integrated Capture and Conversion' in P. Styring, E. A. Quadrelli, & K. Armstrong (eds.), *Carbon Dioxide Utilisation*, pp. 253–272, Elsevier, Amsterdam.
- Pérez-Fortes, M, Schöneberger, JC, Boulamanti, A, & Tzimas, E 2016, 'Methanol synthesis using captured CO<sub>2</sub> as raw material: Techno-economic and environmental assessment' *Applied Energy*, vol. 161, pp. 718–732.
- Perez-Maldonado, RA & Rodrigues, HD 2009, 'Nutritional Characteristics of Sorghums from Queensland and New South Wales for Chicken Meat Production', no. 09, p. 78.
- Peters, M, Köhler, B, Kuckshinrichs, W, Leitner, W, Markewitz, P, & Müller, TE 2011, 'Chemical technologies for exploiting and recycling carbon dioxide into the value chain' *ChemSusChem*, vol. 4, no. 9, pp. 1216–1240.
- Peters, S & Ward, S 2016, *Efficient Costs of New Entrant Ethanol Producers*, vol. 23.
- Petrakopoulou, F & Tsatsaronis, G 2012, 'Production of hydrogen-rich fuels for pre-combustion carbon capture in power plants: A thermodynamic assessment' *International Journal of Hydrogen Energy*, vol. 37, no. 9, pp. 7554–7564.
- Pierre, AC 2012, 'Enzymatic Carbon Dioxide Capture' *ISRN Chemical Engineering*, pp. 1–22.
- Plevin, RJ, O'Hare, , Michael, Jones, AD, Torn, MS, & Gibbs, HK 2010, 'Greenhouse Gas Emissions from Biofuels' Indirect Land Use Change Are Uncertain but May Be Much Greater than Previously Estimated' *Environmental Science & Technology*, vol. 44, no. 21, pp. 8015–8021.
- Pordesimo, LO, Hames, BR, Sokhansanj, S, & Edens, WC 2005, 'Variation in corn stover composition and energy content with crop maturity' *Biomass and Bioenergy*, vol. 28, no. 4, pp. 366–374.

- Portillo, E, Alonso-Fariñas, B, Vega, F, Cano, M, & Navarrete, B 2019, 'Alternatives for oxygen-selective membrane systems and their integration into the oxy-fuel combustion process: A review' *Separation and Purification Technology*, vol. 229, p. 115708.
- PRé Consultants 2019, 'Simapro', Amersfoort, The Netherlands.
- Pulz, O 2001, 'Photobioreactors: production systems for phototrophic microorganisms' *Applied Microbiology and Biotechnology*, vol. 57, no. 3, pp. 287–293.
- Qadir, A, Sharma, M, Parvareh, F, Khalilpour, R, & Abbas, A 2015, 'Flexible dynamic operation of solar-integrated power plant with solvent based post-combustion carbon capture (PCC) process' *Energy Conversion and Management*, vol. 97, pp. 7–19.
- Qiao, J, Liu, Y, Hong, F, & Zhang, J 2014, *A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels Chemical Society Reviews*, vol. 43.
- Quadrelli, EA, Centi, G, Duplan, JL, & Perathoner, S 2011, 'Carbon dioxide recycling: Emerging large-scale technologies with industrial potential' *ChemSusChem*, vol. 4, no. 9, pp. 1194–1215.
- Queensland Government 2017, *Dalby Biorefinery Ltd Advanced Manufacturing | Sustainable Manufacturing in Action*.
- Queensland Government 2021, 'Bulk water prices for South East Queensland', Business Queensland, viewed 16 February 2021, <https://www.business.qld.gov.au/industries/mining-energy-water/water/industry-infrastructure/pricing/bulk-water/prices-seq>.
- Queensland Renewable Energy Expert Panel 2016, *Credible pathways to a 50% renewable energy target for Queensland*.
- Khalilpour, KR, Mumford, K, Zhai, H, Abbas, A, Stevens, G, & Rubin, ES 2015, 'Membrane-based carbon capture from flue gas: A review' *Journal of Cleaner Production*, vol. 103, pp. 286–300.
- Rafiee, A, Khalilpour, KR, Milani, D, & Panahi, M 2018, 'Trends in CO<sub>2</sub> conversion and utilization: A review from process systems Perspective' *Journal of Environmental Chemical Engineering*, vol. 6, no. September, pp. 5771–5794.
- Rajagopal, D, Sexton, SE, Roland-Holst, D, & Zilberman, D 2007, 'Challenge of biofuel: Filling the tank without emptying the stomach?' *Environmental Research Letters*, vol. 2, no. 4.
- Ramsey, E, Sun, Q, Zhang, Z, Zhang, C, & Gou, W 2009, 'Mini-Review: Green sustainable processes using supercritical fluid carbon dioxide' *Journal of Environmental Sciences*, vol. 21, no. 6, pp. 720–726.
- Reich, R, Ziegler, WT, & Rogers, KA 1980, 'Adsorption of Methane, Ethane, and Ethylene Gases and Their Binary and Ternary Mixtures and Carbon Dioxide on Activated Carbon at 212–301 K and Pressures to 35 Atmospheres' *Industrial and Engineering Chemistry Process Design and Development*, vol. 19, no. 3, pp. 336–344.
- Reisinger, A, Meinshausen, M, Manning, M, & Bodeker, G 2010, 'Uncertainties of global warming metrics: CO<sub>2</sub> and CH<sub>4</sub>' *Geophysical Research Letters*, vol. 37, no. 14.
- Ren, D, Ang, BSH, & Yeo, BS 2016, 'Tuning the Selectivity of Carbon Dioxide Electroreduction toward Ethanol on Oxide-Derived Cu<sub>x</sub>Zn Catalysts' *ACS Catalysis*, vol. 6, no. 12, pp. 8239–8247.
- Richter, H, Martin, ME, & Angenent, LT 2013, 'A Two-Stage Continuous Fermentation System for Conversion of Syngas into Ethanol' *Energies*, vol. 6, no. 8, pp. 3987–4000.
- Rickman, M, Pellegrino, J, Hock, J, Shaw, S, & Freeman, B 2013, 'Life-cycle and techno-economic analysis of utility-connected algae systems' *Algal Research*, vol. 2, no. 1, pp. 59–65.
- Rihko-Struckmann, LK, Peschel, A, Hanke-Rauschenbach, R, & Sundmacher, K 2010, 'Assessment of methanol synthesis utilizing exhaust CO<sub>2</sub> for chemical storage of electrical energy' *Industrial and*

- Rogelj, J, Shindell, D, Jiang, K, Fifita, S, Forster, P, Ginzburg, V, Handa, C, Kheshgi, H, Kobayashi, S, Kriegler, E, Mundaca, L, Séférian, R, & Vilariño, MV 2018, 'Mitigation Pathways Compatible with 1.5°C in the Context of Sustainable Development. In: Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathw' *IPCC Special Report Global Warming of 1.5 °C*, p. 82pp.
- Rojas Sanchez, D, Hoadley, AFA, & Khalilpour, KR 2019, 'A multi-objective extended input – output model for a regional economy' *Sustainable Production and Consumption*, vol. 20, pp. 15–28.
- Rojas Sanchez, D, Khalilpour, KR, & Hoadley, AFA 2021, 'How sustainable is CO<sub>2</sub> conversion to ethanol? – a life cycle assessment of a new electrocatalytic carbon utilisation process' *Manuscript Submitted for Publication*.
- Rumayor, M, Dominguez-Ramos, A, & Irabien, A 2019, 'Environmental and economic assessment of the formic acid electrochemical manufacture using carbon dioxide: Influence of the electrode lifetime' *Sustainable Production and Consumption*, vol. 18, pp. 72–82.
- Saba, SM, Müller, M, Robinius, M, & Stolten, D 2018, 'The investment costs of electrolysis – A comparison of cost studies from the past 30 years' *International Journal of Hydrogen Energy*, vol. 43, no. 3, pp. 1209–1223.
- Sakakura, T, Choi, J-C, & Yasuda, H 2007, 'Transformation of Carbon Dioxide' *Chemical Reviews*, vol. 107, no. 6, pp. 2365–2387.
- Sakimoto, KK, Kornienko, N, & Yang, P 2017, 'Cyborgian material design for solar fuel production: The emerging photosynthetic biohybrid systems' *Accounts of Chemical Research*, vol. 50, no. 3, pp. 476–481.
- San Cristóbal, JR 2010, 'An environmental/input-output linear programming model to reach the targets for greenhouse gas emissions set by thekyoto protocol' *Economic Systems Research*, vol. 22, no. 3, pp. 223–236.
- Sánchez, M, Amores, E, Abad, D, Rodríguez, L, & Clemente-Jul, C 2020, 'Aspen Plus model of an alkaline electrolysis system for hydrogen production' *International Journal of Hydrogen Energy*, vol. 45, no. 7, pp. 3916–3929.
- Sathre, R, Chester, M, Cain, J, & Masanet, E 2012, 'A framework for environmental assessment of CO<sub>2</sub> capture and storage systems' *Energy*, vol. 37, no. 1, pp. 540–548.
- Saunders, J, Izydorczyk, M, & B., D 2011, 'Limitations and Challenges for Wheat-Based Bioethanol Production' in M. A. Dos Santos Bernardes (ed.), *Economic Effects of Biofuel Production*, 1st edn, InTech.
- Schakel, W, Oreggioni, G, Singh, B, Strømman, A, & Ramírez, A 2016, 'Assessing the techno-environmental performance of CO<sub>2</sub>utilization via dry reforming of methane for the production of dimethyl ether' *Journal of CO<sub>2</sub> Utilization*, vol. 16, pp. 138–149.
- Schmidt, O, Gambhir, A, Staffell, I, Hawkes, A, Nelson, J, & Few, S 2017, 'Future cost and performance of water electrolysis: An expert elicitation study' *International Journal of Hydrogen Energy*, vol. 42, no. 52, pp. 30470–30492.
- Searchinger, T, Heimlich, R, Houghton, RA, Dong, F, Elobeid, A, Fabiosa, J, Tokgoz, S, Hayes, D, & Yu, TH 2008, 'Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land-use change' *Science*, vol. 319, no. 5867, pp. 1238–1240.
- Semelsberger, TA, Borup, RL, & Greene, HL 2006, 'Dimethyl ether (DME) as an alternative fuel' *Journal of Power Sources*, vol. 156, no. 2, pp. 497–511.

- Shamsul, NS, Kamarudin, SK, Rahman, NA, & Kofli, NT 2014, 'An overview on the production of bio-methanol as potential renewable energy' *Renewable and Sustainable Energy Reviews*, vol. 33, pp. 578–588.
- Sharifzadeh, M, Wang, L, & Shah, N 2015, 'Integrated biorefineries: CO<sub>2</sub> utilization for maximum biomass conversion' *Renewable and Sustainable Energy Reviews*, vol. 47, pp. 151–161.
- Sharp, K 2020, *Personal communication*.
- Shine, KP, Derwent, RG, Wuebbles, DJ, & Morcrette, J-J 1990, *Climate Change: The IPCC Scientific Assessment. Report prepared for Intergovernmental Panel on Climate Change by Working Group I. Chapter 2. Radiative forcing of climate* *Climate Change: The IPCC Scientific Assessment. Report prepared for Intergovernmental Panel on Climate Change by Working Group I*.
- Sifat, NS & Haseli, Y 2019, 'A Critical Review of CO<sub>2</sub> Capture Technologies and Prospects for Clean Power Generation' *Energies*, vol. 12, no. 21.
- Siirila, ER, Navarre-Sitchler, AK, Maxwell, RM, & McCray, JE 2012, 'A quantitative methodology to assess the risks to human health from CO<sub>2</sub> leakage into groundwater' *Advances in Water Resources*, vol. 36, pp. 146–164.
- Simons, A & Bauer, C 2015, 'A life-cycle perspective on automotive fuel cells' *Applied Energy*, vol. 157, pp. 884–896.
- Sisler, J, Khan, S, Ip, AH, Schreiber, MW, Jaffer, SA, Bobicki, ER, Dinh, CT, & Sargent, EH 2021, 'Ethylene Electrosynthesis: A Comparative Techno-economic Analysis of Alkaline vs Membrane Electrode Assembly vs CO<sub>2</sub>-CO-C<sub>2</sub>H<sub>4</sub> Tandems' *ACS Energy Letters*, pp. 997–1002.
- Skone, T, Mutcheck, M, Krynock, M, Cooney, G, Pegallapati, A, Rai, S, Chou, J, Carlson, D, Jamieson, M, Venkatesh, A, Littlefield, J, Zaimes, GG, Roman-white, S, & Dale, E 2019, *Carbon Dioxide Utilization Life Cycle Analysis Guidance for the U.S. DOE Office of Fossil Energy*.
- Smith, R & Linnhoff, B 1988, 'Design of separators in the context of overall processes' *Chem. Eng. Res. Des.*, vol. 66, no. 3, pp. 195–228.
- Smolinka, T, Günther, M, & Garche, J 2011, *Stand und Entwicklungspotenzial der Wasserelektrolyse zur Herstellung von Wasserstoff aus regenerativen Energien*, Fraunhofer ISE;
- Solidia Technologies n.d., 'Solidia Technologies', viewed 19 November 2018, <https://www.solidiatech.com>.
- Song, Y, Peng, R, Hensley, DK, Bonnesen, P V., Liang, L, Wu, Z, Meyer, HM, Chi, M, Ma, C, Sumpter, BG, & Rondinone, AJ 2016, 'High-Selectivity Electrochemical Conversion of CO<sub>2</sub> to Ethanol using a Copper Nanoparticle/N-Doped Graphene Electrode' *ChemistrySelect*, vol. 1, no. 19, pp. 6055–6061.
- Spinner, NS, Vega, JA, & Mustain, WE 2012, 'Recent progress in the electrochemical conversion and utilization of CO<sub>2</sub>' *Catalysis Science and Technology*, vol. 2, no. 1, pp. 19–28.
- St Clair, JH & Simister, WF 1983, 'Process to recover CO<sub>2</sub> from flue gas gets first large-scale tryout in Texas' *Oil Gas J.*, vol. 81, no. 7.
- State of Queensland 2016, *Queensland Biofutures 10-Year Roadmap and Action Plan*.
- State of Queensland 'Liquid Fuel Supply Act 1984', (2017).
- Sternberg, A, Jens, CM, & Bardow, A 2017, 'Life cycle assessment of CO<sub>2</sub>-based C<sub>1</sub>-chemicals' *Green Chemistry*, vol. 19, no. 9, pp. 2244–2259.
- Stradling, R, Williams, J, Hamje, H, & Rickeard, D 2016, 'Effect of Octane on Performance, Energy Consumption and Emissions of Two Euro 4 Passenger Cars' *Transportation Research Procedia*, vol. 14, pp. 3159–3168.
- Stumm, W & Morgan, JJ 1995, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd

editio.

- Styring, P 2015a, 'Carbon Dioxide Capture Agents and Processes' in P. Styring, E. A. Quadrelli, & K. Armstrong (eds.), *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, 1st edn, pp. 19–32, Elsevier, Amsterdam.
- Styring, P 2015b, 'Chapter 2 - Carbon Dioxide Capture Agents and Processes' in P. Styring, E. A. Quadrelli, & K. Armstrong (eds.), *Carbon Dioxide Utilisation*, pp. 19–32, Elsevier, Amsterdam.
- Styring, P, Jansen, D, de Coninck, H, Reith, H, & Armstrong, K 2011, *Carbon Capture and Utilisation in the green economy Centre for Low Carbon Futures 2011 and CO2Chem Publishing 2012*.
- Styring, P, Quadrelli, EA, & Armstrong, K 2015a, *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, Elsevier.
- Styring, P, Quadrelli, EA, & Armstrong, K 2015b, 'Preface' in P. Styring, E. A. Quadrelli, & K. Armstrong (eds.), *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, 1st edn, pp. xv–xxiv, Elsevier, Amsterdam.
- Sun, J & Wang, Y 2014, 'Recent advances in catalytic conversion of ethanol to chemicals' *ACS Catalysis*, vol. 4, no. 4, pp. 1078–1090.
- Sunfire 2019, 'Carbon-neutral fuels from air and electric power', viewed 19 November 2020, <https://www.sunfire.de/en/news/detail/carbon-neutral-fuels-from-air-and-electric-power>.
- Supasitmongkol, S & Styring, P 2010, 'High CO<sub>2</sub> solubility in ionic liquids and a tetraalkylammonium-based poly(ionic liquid)' *Energy & Environmental Science*, vol. 3, no. 12, p. 1961.
- Surisetty, VR, Dalai, AK, & Kozinski, J 2011, 'Alcohols as alternative fuels: An overview' *Applied Catalysis A: General*, vol. 404, no. 1–2, pp. 1–11.
- Syed, A 2014, *Australian Energy Projections to 2049-50 BREE*.
- Tan, YC, Lee, KB, Song, H, & Oh, J 2020, 'Modulating Local CO<sub>2</sub> Concentration as a General Strategy for Enhancing C–C Coupling in CO<sub>2</sub> Electroreduction' *Joule*, vol. 4, no. 5, pp. 1104–1120.
- Terwel, BW, Harinck, F, Ellemers, N, & Daamen, DDL 2011, 'Going beyond the properties of CO<sub>2</sub> capture and storage (CCS) technology: How trust in stakeholders affects public acceptance of CCS' *International Journal of Greenhouse Gas Control*, vol. 5, no. 2, pp. 181–188.
- Thomas, BA & Azevedo, IL 2013, 'Estimating direct and indirect rebound effects for U.S. households with input-output analysis Part 1: Theoretical framework' *Ecological Economics*, vol. 86, pp. 199–210.
- Thybaud, N & Lebain, D 2010, 'Panorama des voies de valorisation du CO<sub>2</sub>' *Alcimed*, p. 190.
- Timmer, MP, Dietzenbacher, E, Los, B, Stehrer, R, & de Vries, GJ 2015, 'An Illustrated User Guide to the World Input-Output Database: The Case of Global Automotive Production' *Review of International Economics*, vol. 23, pp. 575–605.
- Trading Economics 2021, 'Ethanol 2005-2021 Data', viewed 20 April 2021, <https://tradingeconomics.com/commodity/ethanol>.
- Turner, JWG, Lewis, AGJ, Akehurst, S, Brace, CJ, Verhelst, S, Vancoillie, J, Sileghem, L, Leach, F, & Edwards, PP 2018, 'Alcohol fuels for spark-ignition engines: Performance, efficiency and emission effects at mid to high blend rates for binary mixtures and pure components' *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering*, vol. 232, no. 1, pp. 36–56.
- Turton, R, Bailie, RC, Whiting, WB, & Shaeiwitz, JA 2008, *Analysis, Synthesis and Design of Chemical Processes*, 5th editio, Pearson Education.
- UN General Assembly 'Transforming our world: the 2030 Agenda for Sustainable Development', (2015).

- UNFCCC 1998, *Kyoto Protocol To the United Nations Framework Review of European Community and International Environmental Law*, vol. 7, doi:/10.1111/1467-9388.00150.
- UNFCCC 2012, *Doha Amendment to the Kyoto Protocol Kyoto Protocol To the United Nations Framework*, doi:/10.1289/image.ehp.v119.i03.
- UNFCCC 2015, *Registration of Paris Agreement*, vol. 21.
- United Petroleum n.d., 'Dalby Gas Pipeline', viewed 24 October 2020, <https://www.unitedpetroleum.com.au/dalby-bio-refinery/dalby-gas-pipeline/>.
- United Petroleum 2020, 'Safety Data Sheet (LQA78) for industrial grade ethanol', United Petroleum Pty Ltd.
- Utgikar, V & Thiesen, T 2006, 'Life cycle assessment of high temperature electrolysis for hydrogen production via nuclear energy' *International Journal of Hydrogen Energy*, vol. 31, no. 7, pp. 939–944.
- van Sluisveld, MAE, Martínez, SH, Daioglou, V, & van Vuuren, DP 2016, 'Exploring the implications of lifestyle change in 2°C mitigation scenarios using the IMAGE integrated assessment model' *Technological Forecasting and Social Change*, vol. 102, pp. 309–319.
- Viebahn, P, Scholz, A, & Zelt, O 2019, 'German Energy Research Program — Results of a Multi-Dimensional Analysis' *Energies*, vol. 18, pp. 1–27.
- Vohra, M, Manwar, J, Manmode, R, Padgilwar, S, & Patil, S 2014, 'Bioethanol production: Feedstock and current technologies' *Journal of Environmental Chemical Engineering*, vol. 2, no. 1, pp. 573–584.
- von der Assen, N 2015, *From life-cycle assessment towards life-cycle design of carbon dioxide capture and utilization*, doctoral thesis, Rheinisch-Westfälischen Technischen Hochschule Aachen University.
- von der Assen, N, Jung, J, & Bardow, A 2013, 'Life-cycle assessment of carbon dioxide capture and utilization: avoiding the pitfalls' *Energy & Environmental Science*, vol. 6, no. 9, p. 2721.
- von der Assen, N, Lafuente, AML, Peters, M, & Bardow, A 2015, 'Environmental Assessment of CO<sub>2</sub> Capture and Utilisation' in P. Styring, E. A. Quadrelli, & K. Armstrong (eds.), *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, 1st edn, Elsevier, Amsterdam.
- von der Assen, N, Voll, P, Peters, M, & Bardow, A 2014, 'Life cycle assessment of CO<sub>2</sub> capture and utilization: A tutorial review' *Chemical Society Reviews*, vol. 43, no. 23, pp. 7982–7994.
- von Storch, H, Roeb, M, Stadler, H, Sattler, C, Bardow, A, & Hoffschmidt, B 2016, 'On the assessment of renewable industrial processes: Case study for solar co-production of methanol and power' *Applied Energy*, vol. 183, pp. 121–132.
- Wall, T & Stanger, R 2011, 'Industrial scale oxy-fuel technology demonstration' in L. Zheng (ed.), *Oxy-Fuel Combustion for Power Generation and Carbon Dioxide (CO<sub>2</sub>) Capture*, pp. 54–76, Woodhead Publishing.
- Wang, J, Huang, L, Yang, R, Zhang, Z, Wu, J, Gao, Y, Wang, Q, O'Hare, D, & Zhong, Z 2014, 'Recent advances in solid sorbents for CO<sub>2</sub> capture and new development trends' *Energy Environ. Sci.*, vol. 7, no. 11, pp. 3478–3518.
- Wang, T, Lackner, KS, & Wright, A 2011, 'Moisture Swing Sorbent for Carbon Dioxide Capture from Ambient Air' *Environmental Science & Technology*, vol. 45, no. 15, pp. 6670–6675.
- Wang, X, Wang, Z, García de Arquer, FP, Dinh, CT, Ozden, A, Li, YC, Nam, DH, Li, J, Liu, YS, Wicks, J, Chen, Z, Chi, M, Chen, B, Wang, Y, Tam, J, Howe, JY, Proppe, A, Todorović, P, Li, F, Zhuang, TT, Gabardo, CM, Kirmani, AR, McCallum, C, Hung, SF, Lum, Y, Luo, M, Min, Y, Xu, A, O'Brien, CP, Stephen, B, Sun, B, Ip, AH, Richter, LJ, Kelley, SO, Sinton, D, & Sargent, EH 2020, 'Efficient

- electrically powered CO<sub>2</sub>-to-ethanol via suppression of deoxygenation' *Nature Energy*, vol. 5, no. 6, pp. 478–486.
- Wang, X, Wang, Z, Zhuang, T-T, Dinh, C-T, Li, J, Nam, D-H, Li, F, Huang, C-W, Tan, C-S, Chen, Z, Chi, M, Gabardo, CM, Seifitokaldani, A, Todorović, P, Proppe, A, Pang, Y, Kirmani, AR, Wang, Y, Ip, AH, Richter, LJ, Scheffel, B, Xu, A, Lo, S-C, Kelley, SO, Sinton, D, & Sargent, EH 2019, 'Efficient upgrading of CO to C<sub>3</sub> fuel using asymmetric C-C coupling active sites' *Nature Communications*, vol. 10, no. 1, p. 5186.
- Ward, H, Burger, M, Chang, Y-J, Fürstmann, P, Neugebauer, S, Radebach, A, Sproesser, G, Pittner, A, Rethmeier, M, Uhlmann, E, & Steckel, JC 2017, 'Assessing carbon dioxide emission reduction potentials of improved manufacturing processes using multiregional input output frameworks' *Journal of Cleaner Production*, vol. 163, no. Supplement C, pp. 154–165.
- Waterfind 2019, *Australian Water Markets Annual Report*.
- Weekes, DM, Salvatore, DA, Reyes, A, Huang, A, & Berlinguette, CP 2018, 'Electrolytic CO<sub>2</sub> Reduction in a Flow Cell' *Accounts of Chemical Research*, vol. 51, no. 4, pp. 910–918.
- Weidema, BP 2011, 'Stepping Stones From Life Cycle Assessment to Adjacent Assessment Techniques' *Journal of Industrial Ecology*, vol. 15, no. 5, pp. 658–661.
- Weisenberger, S & Schumpe, A 1996, 'Estimation of Gas Solubilities in Salt Solutions at Temperatures from 273 K to 363 K' *AIChE Journal*, vol. 42, no. 1, pp. 298–300.
- Wernet, G, Bauer, C, Steubing, B, Reinhard, J, Moreno-Ruiz, E, & Weidema, B 2016, 'The ecoinvent database version 3 (part I): overview and methodology' *International Journal of Life Cycle Assessment*, vol. 21, no. 9, pp. 1218–1230.
- Wernet, G, Lérová, T, Bourgault, G, Valsasina, L, Fitzgerald, D, & Moreno Ruiz, E 2017, *Data on Production of Chemicals created for the EU Product Environmental Footprint (PEF) pilot phase implementation*.
- Wernet, G, Papadokonstantakis, S, Hellweg, S, & Hungerbühler, K 2009, 'Bridging data gaps in environmental assessments: Modeling impacts of fine and basic chemical production' *Green Chem.*, vol. 11, no. 11, pp. 1826–1831.
- West, GR 1999, *Notes on some Common Misconceptions in Input-Output Impact Methodology*.
- Wienchol, P, Szłęk, A, & Ditaranto, M 2020, 'Waste-to-energy technology integrated with carbon capture – Challenges and opportunities' *Energy*, vol. 198, p. 117352.
- Wijesiri, RP, Knowles, GP, Yeasmin, H, Hoadley, AFA, & Chaffee, AL 2019, 'Technoeconomic Evaluation of a Process Capturing CO<sub>2</sub> Directly from Air' *Processes*, vol. 7, no. 8, p. 503.
- Williams, ED, Weber, CL, & Hawkins, TR 2009, 'Hybrid Framework for Managing Uncertainty in Life Cycle Inventories' *Journal of Industrial Ecology*, vol. 13, no. 6, pp. 928–944.
- Wisiz, MW, Antonelli, R, & Ragi, EG 1981, 'High Performance Trays and Heat Exchangers in Heat Pumped Distillation Columns' in *Third Industrial Energy Technology Conference*, pp. 91–96, Houston, TX.
- Wood, R 2009, 'Structural decomposition analysis of Australia's greenhouse gas emissions' *Energy Policy*, vol. 37, no. 11, pp. 4943–4948.
- Wood, R & Dey, CJ 2009, 'Australia's carbon footprint' *Economic Systems Research*, vol. 21, no. 3, pp. 243–266.
- Wood, R & Lenzen, M 2009, 'Aggregate measures of complex economic structure and evolution a review and case study' *Journal of Industrial Ecology*, vol. 13, no. 2, pp. 264–283.

- World Commission on Environment and Development 1987, *Our common future*, Oxford University Press, Oxford.
- Wu, J, Sharma, PP, Harris, BH, & Zhou, XD 2014, 'Electrochemical reduction of carbon dioxide: IV dependence of the Faradaic efficiency and current density on the microstructure and thickness of tin electrode' *Journal of Power Sources*, vol. 258, pp. 189–194.
- Xie, J & Saltzman, S 2000, 'Environmental Policy Analysis: An Environmental Computable General-Equilibrium Approach for Developing Countries' *Journal of Policy Modeling*, vol. 22, no. 4, pp. 453–489.
- Yacout, DMM, Abd El-Kawi, MA, & Hassouna, MS 2016, 'Cradle to gate environmental impact assessment of acrylic fiber manufacturing' *International Journal of Life Cycle Assessment*, vol. 21, no. 3, pp. 326–336.
- Zandvoort, I van, Ras, EJ, de Graaf, R, & Krishna, R 2020, 'Using transient breakthrough experiments for screening of adsorbents for separation of C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub> mixtures' *Separation and Purification Technology*, vol. 241, no. October 2019, p. 116706.
- Zhai, H & Rubin, ES 2018, 'Systems Analysis of Physical Absorption of CO<sub>2</sub> in Ionic Liquids for Pre-Combustion Carbon Capture' *Environmental Science & Technology*, vol. 52, no. 8, pp. 4996–5004.
- Zhang, Fengtao, Zhang, H, & Liu, Z 2019, 'Recent advances in electrochemical reduction of CO<sub>2</sub>' *Current Opinion in Green and Sustainable Chemistry*, vol. 16, pp. 77–84.
- Zhang, Fengxiang, Zhang, H, & Qu, C 2011, 'Imidazolium functionalized polysulfone anion exchange membrane for fuel cell application' *Journal of Materials Chemistry*, vol. 21, no. 34, pp. 12744–12752.
- Zhang, X, Bauer, C, Mutel, CL, & Volkart, K 2017, 'Life Cycle Assessment of Power-to-Gas: Approaches, system variations and their environmental implications' *Applied Energy*, vol. 190, pp. 326–338.
- Zhao, M, Minett, AI, & Harris, AT 2013, 'A review of techno-economic models for the retrofitting of conventional pulverised-coal power plants for post-combustion capture (PCC) of CO<sub>2</sub>' *Energy and Environmental Science*, vol. 6, no. 1, pp. 25–40.
- Zhong, H, Fujii, K, Nakano, Y, & Jin, F 2015, 'Effect of CO<sub>2</sub> bubbling into aqueous solutions used for electrochemical reduction of CO<sub>2</sub> for energy conversion and storage' *Journal of Physical Chemistry C*, vol. 119, no. 1, pp. 55–61.
- Zhou, H, Liu, K, Li, H, Cao, M, Fu, J, Gao, X, Hu, J, Li, W, Pan, H, Zhan, J, Li, Q, Qiu, X, & Liu, M 2019, 'Recent advances in different-dimension electrocatalysts for carbon dioxide reduction' *Journal of Colloid and Interface Science*, vol. 550, no. May 2018, pp. 17–47.
- Zhou, M, Liu, Y, Feng, S, Liu, Y, & Lu, Y 2018, 'Decomposition of rebound effect: An energy-specific, general equilibrium analysis in the context of China' *Applied Energy*, vol. 221, no. April, pp. 280–298.
- Zhuang, TT, Pang, Y, Liang, ZQ, Wang, Z, Li, Y, Tan, CS, Li, J, Dinh, CT, De Luna, P, Hsieh, PL, Burdyny, T, Li, HH, Liu, M, Wang, Y, Li, F, Proppe, A, Johnston, A, Nam, DH, Wu, ZY, Zheng, YR, Ip, AH, Tan, H, Chen, LJ, Yu, SH, Kelley, SO, Sinton, D, & Sargent, EH 2018, 'Copper nanocavities confine intermediates for efficient electrosynthesis of C<sub>3</sub> alcohol fuels from carbon monoxide' *Nature Catalysis*, vol. 1, no. 12, pp. 946–951.
- Zimmerman, A, Wunderlich, J, Buchner, G, Müller, L, Armstrong, K, Michailos, S, Marxen, A, Naims, H, Mason, F, Stokes, G, & Williams, E 2018, *Techno-Economic Assessment & Life-Cycle Assessment Guidelines for CO<sub>2</sub> Utilization*, doi:10.3998/2027.42/145436.
- Zimmermann, AW, Müller, L, Wang, Y, Langhorst, T, Wunderlich, J, Marxen, A, Armstrong, K, Buchner, G, Kätelhön, A, Bachmann, M, Sternberg, A, Michailos, S, McCord, S, Zaragoza, AV, Naims, H,



- Cremonese, L, Strunge, T, Faber, G, Mangin, C, Olfe-Kräutlein, B, Styring, P, Schomäcker, R, Bardow, A, & Sick, V 2020, 'Techno-Economic Assessment & Life Cycle Assessment Guidelines for CO2 Utilization (Version 1.1)', p. 185.
- Zoulas, M, Glöckner, R, Lymberopoulos, N, Vosseler, I, Tsoutsos, T, Mydske, HJ, Brodin, M, & Taylor, P 2004, *Market potential analysis for the introduction of hydrogen energy technology in stand-alone power systems*.
- Zuccotti, GV & Fabiano, V 2011, 'Safety issues with ethanol as an excipient in drugs intended for pediatric use' *Expert Opinion on Drug Safety*, vol. 10, no. 4, pp. 499–502.

# Appendix A

Table A shows the correspondence between the aggregated nomenclature in the case study of the extended input-output analysis in Chapter 3, the International Standard Industrial Classification of all economic activities (ISIC), and the Australian and New Zealand Standard Industrial Classification (ANZSIC) (ABS 2006) (cat. no. 1292.0).

Table A. Correspondence of industry sectors in different classifications

Aggregated Classification		ISIC Rev. 3.1		ISIC Rev. 4		ANZSIC	
Abbreviation	Description	Code	Description	Code	Description	Code	Description
Agriculture	Agriculture, Forestry and Fishing	secA1B	Agriculture, Hunting, Forestry and Fishing	A01	Crop and animal production, hunting and related service activities	A01	Agriculture
				A02	Forestry and logging	A04	Fishing, Hunting and Trapping
				A03	Fishing and aquaculture	A05	Agriculture, Forestry and Fishing Support Services
						A03	Forestry and Logging
Mining	Mining	secC	Mining and Quarrying	B	Mining and quarrying	A02	Aquaculture
Food&Tobacco	Food, Beverage and Tobacco	sec15t16	Food, Beverages and Tobacco	C10-C12	Manufacture of food products, beverages and tobacco products	A04	Fishing, Hunting and Trapping
Textile	Textile, Leather, Clothing and Footwear	sec17t18 sec19	Textiles and Textile Products Leather, Leather and Footwear	C13-C15	Manufacture of textiles, wearing apparel and leather products	C13	Textile, Leather, Clothing and Footwear Manufacturing
Wood Products	Wood Products	sec20	Wood and Products of Wood and Cork	C16	Manufacture of wood and of products of wood and cork, except furniture; manufacture of articles of straw and plaiting materials	C14	Wood Product Manufacturing
Pulp&Paper	Pulp, Paper, Printing and Publishing	sec21t22	Pulp, Paper, Paper Products, Printing and Publishing	C17	Manufacture of paper and paper products	C15	Pulp, Paper and Converted Paper Product Manufacturing
				C18	Printing and reproduction of recorded media	C16	Printing (including the reproduction of Recorded Media)
Petro.&Nuclear	Coke, Petroleum products and Nuclear Fuel	sec23	Coke, Refined Petroleum and Nuclear Fuel	J58	Publishing activities	J54	Publishing (except Internet and Music Publishing)
Chem.&Pharm.	Chemicals and Pharmaceutical Products	sec24	Chemicals and Chemical Products	C19	Manufacture of coke and refined petroleum products	C17	Petroleum and Coal Product Manufacturing
				C20	Manufacture of chemicals and chemical products	C18	Basic Chemical and Chemical Product Manufacturing
Plastics	Rubbers and Plastics	sec25	Rubber and Plastics	C21	Manufacture of basic pharmaceutical products and pharmaceutical preparations	C184	Pharmaceutical and Medicinal Product Manufacturing
Non-metals	Non-Metallic Mineral	sec26	Other Non-Metallic Mineral	C22	Manufacture of rubber and plastic products	C19	Polymer Product and Rubber Product Manufacturing
Metals	Basic and Fabricated Metals	sec27t28	Basic Metals and Fabricated Metal	C23	Manufacture of other non-metallic mineral products	C20	Non-Metallic Mineral Product Manufacturing
				C24	Manufacture of basic metals	C21	Primary Metal and Metal Product Manufacturing
Elec.&Opt.Eq.	Electrical and Optical Equipment	sec30t33	Electrical and Optical Equipment	C25	Manufacture of fabricated metal products, except machinery and equipment	C22	Fabricated Metal Product Manufacturing
				C26	Manufacture of computer, electronic and optical products	C24	Machinery and Equipment Manufacturing
Oth. Mach.	Other Machinery	sec29	Machinery, Nec	C27	Manufacture of electrical equipment	C243	Electrical Equipment Manufacturing
				C28	Manufacture of machinery and equipment n.e.c.	C249	Other Machinery and Equipment Manufacturing
				C33	Repair and installation of machinery and equipment	S94	Repair and Maintenance

Table A. Correspondence of industry sectors in different classifications (*continued*)

Aggregated Classification		ISIC Rev. 3.1		ISIC Rev. 4		ANZSIC	
Abbreviation	Description	Code	Description	Code	Description	Code	Description
Trsp. Mfg.	Transport Manufacturing	sec34t35	Transport Equipment	C29 C30	Manufacture of motor vehicles, trailers and semi-trailers Manufacture of other transport equipment	C231 C239	Motor Vehicle and Motor Vehicle Part Manufacturing Other Transport Equipment Manufacturing
Oth. Mfg.	Other Manufacturing; Recycling	sec36t37	Manufacturing, Nec; Recycling	C31_C32	Manufacture of furniture; other manufacturing	C25	Furniture and Other Manufacturing
Utilities Supply	Electricity, Gas and Water Supply	secE	Electricity, Gas and Water Supply	D35 E36	Electricity, gas, steam and air conditioning supply Water collection, treatment and supply	D26 D27 D28	Electricity Supply Gas Supply Water Supply, Sewerage and Drainage Services
Waste Mgt.	Waste Collection, Treatment and Disposal Services; Other Social and Personal Services	secO	Other Community, Social and Personal Services	E37-E39 R_S	Sewerage; waste collection, treatment and disposal activities; materials recovery; remediation activities and other waste management services Other service activities	D29 R S	Waste Collection, Treatment and Disposal Services Arts and Recreation Services Other Services
Construction	Construction	secF	Construction	F	Construction	E	Construction
Motor Whole.	Motor Vehicle Wholesaling	sec50	Sale, Maintenance and Repair of Motor Vehicles and Motorcycles; Retail Sale of Fuel	G45	Wholesale and retail trade and repair of motor vehicles and motorcycles	F35 G40	Motor Vehicle and Motor Vehicle Parts Wholesaling Fuel Retailing
Oth. Whole.	Other Wholesaling	sec51	Wholesale Trade and Commission Trade, Except of Motor Vehicles and Motorcycles	G46	Wholesale trade, except of motor vehicles and motorcycles	F33 F34 F36 F37 F38	Basic Material Wholesaling Machinery and Equipment Wholesaling Grocery, Liquor and Tobacco Product Wholesaling Other Goods Wholesaling Commission-Based Wholesaling
Retail Trade	Retail Trade	sec52	Retail Trade, Except of Motor Vehicles and Motorcycles; Repair of Household Goods	G47	Retail trade, except of motor vehicles and motorcycles	G41 G42 G43	Food Retailing Other Store-Based Retailing Non-Store Retailing and Retail Commission Based Buying and/or Selling
Land Trsp.	Inland Transport	sec60	Inland Transport	H49	Land transport and transport via pipelines	I46 I47	Road Transport Rail Transport
Water Trsp.	Water Transport	sec61	Water Transport	H50	Water transport	I48	Water Transport
Air Trsp.	Air Transport	sec62	Air Transport	H51	Air transport	I49	Air and Space Transport
Supp. Trsp.	Supporting Transport Activities; Warehousing	sec63	Other Supporting and Auxiliary Transport Activities; Activities of Travel Agencies	H52	Warehousing and support activities for transportation	I50 I52 I53	Other Transport Transport Support Services Warehousing and Storage Services

Table A. Correspondence of industry sectors in different classifications (continued)

Aggregated Classification		ISIC Rev. 3.1		ISIC Rev. 4		ANZSIC	
Abbreviation	Description	Code	Description	Code	Description	Code	Description
Telecomms.	Post and Telecommunications	sec64	Post and Telecommunications	H53 J61	Postal and courier activities Telecommunications	I51 J58	Postal and Courier Pick-up and Delivery Services Telecommunications Services
Hotel Services	Accommodation and Food Services	secH	Hotels and Restaurants	I	Accommodation and food service activities	H	Accommodation and Food Services
Finance&Ins.	Finance and Insurance Services	secJ	Financial Intermediation	K64	Financial service activities, except insurance and pension funding	K62	Finance
				K65	Insurance, reinsurance and pension funding, except compulsory social security	K63	Insurance and Superannuation Funds
				K66	Activities auxiliary to financial services and insurance activities	K64	Auxiliary Finance and Insurance Services
Real Estate	Real Estate Activities	sec70	Real Estate Activities	L68	Real estate activities	L67	Property Operators and Real Estate Services
Prof. Services	Professional, Scientific, Technical and Information Services	sec71t74	Renting of M&Eq and Other Business Activities	J59_J60	Motion picture, video and television programme production, sound recording and music publishing activities; programming and broadcasting activities	J55 J66 J67	Motion Picture and Sound Recording Activities Broadcasting (except Internet) Internet Publishing and Broadcasting
				J62_J63	Computer programming, consultancy and related activities; information service activities	J59 J60	Internet Service Providers, Web Search Portals and Data Processing Services Library and Other Information Services
				M69_M70	Legal and accounting activities; activities of head offices; management consultancy activities	M693	Legal and Accounting Services
				M71	Architectural and engineering activities; technical testing and analysis	M696	Management and Related Consulting Services
				M72	Scientific research and development	M692	Architectural, Engineering and Technical Services
				M73	Advertising and market research	M691	Scientific Research Services
				M74_M75	Other professional, scientific and technical activities; veterinary activities	M694 M695 M697	Advertising Services Market Research and Statistical Services Veterinary Services
				N	Administrative and support service activities	M699	Other Professional, Scientific and Technical Services
				O84	Public administration and defence; compulsory social security	N	Administrative and Support Services
				P85	Education	O	Public Administration and Safety
Defence	Public Administration and Safety	secL	Public Admin and Defence; Compulsory Social Security	O84	Public administration and defence; compulsory social security	P	Education and Training
Education	Education	secM	Education	P85	Education	Q	Health Care and Social Assistance
Healthcare	Health Care and Social Assistance	secN	Health and Social Work	Q	Human health and social work activities	Q	Private Households Employing Staff and Undifferentiated Goods- and Service-Producing Activities of Households for Own Use
Households	Private Households with Employed Persons	secP	Private Households with Employed Persons	T	Activities of households as employers; undifferentiated goods- and services-producing activities of households for own use	S96	Undifferentiated Goods- and Service-Producing Activities of Households for Own Use

# Appendix B

The following appendix provides a detailed description and account of the inventories used in the life cycle assessment in Chapter 4 and Chapter 5, relevant figures and tables, and supporting information.

## General inventory considerations

All background processes for the life cycle inventory (LCI) data come from two databases: the Australian Life Cycle Initiative (AusLCI) database V1.35 (Australian Life Cycle Assessment Society 2020) and ecoinvent 3.5 (Wernet et al. 2016).

Unless otherwise noted, different processes assume Australian conditions. Key transportation distances were modified to better represent the area of study. However, general or universal processes may be based on transportation distances for materials in Europe, as reported in the ecoinvent database. Whenever distances are unknown, transport is assumed to be a standard distance of 100km for Lorry >16t and 600km for freight rail, as used throughout the AusLCI database. Whenever a transport requirement is not directly input, it means it is included within the process of the material requirement itself.

Waste and emissions of the end of life of each manufacture process are included in full within its inventory. When a process needs an equipment or chemical manufactured, its required mass, unit, area, or volume will be normalised according to its lifetime. Operation hours for plants are assumed 8,000 hours in a year, as per industry standard.

## B1. Electrolyser stack

The electrolyser was modelled according to the description in Chapter 5, section 1.4.1.2. It was first scaled-up to 2 m<sup>2</sup>, which is the area of the electrode in an advanced large-scale alkaline electrolyser described in Koj *et al.* (2015). The process for scaling the inventory requirements is described in Section B1.1 and in subsequent inventories for subcomponents. Then, the electrolyser was scaled-out by creating stacks to match the output of the reference system. Up to 15,429 assembled electrolysers are needed to produce the necessary ethanol flow.

The electrolyser stack was assumed to be rows of assembled electrolysers stacks. The design of the electrolyser assembly allows stacking them as a wall, on one side inputs of electrolyte and gas and, on the other, its corresponding outputs. To reinforce the modular advantage of these electrolyser cells, stacks were designed to fit into a standard 40ft container (12.2 m x 2.4 m x 2.6 m). With these dimensions, 31 containers are needed, each with seven electrolysers in a row and 72 stacked in each column. The area needed within the plant is calculated from the number of containers needed, assuming three can be stacked on top of each other. An added 15% of this area is added to cover the space needed for pumps, valves, and pipelines. This total area required is linked to transformation, while the occupation is based on the lifetime of the entire stack.

Alkaline electrolysis cell stacks can have a lifetime of 60,000 – 90,000 hours (Schmidt *et al.* 2017). To take a conservative approach and given that voltage degradation starts to happen at the lower end of that range in low-temperature alkaline systems (Bertuccioli *et al.* 2014), the lifetime of the electrolyser stack was assumed 60,000 hours. Therefore, the lifetimes of the membrane, gas diffusion layer, anode, and electrolyte will be 60,000 hours of operation, consistent with the LCA by Rumayor *et al.* (2019). The lifetime of the frame and other components outside of the stack are

assumed 20 years, which is the lower end of the lifetime of alkaline electrolysis systems described in Carmo *et al.* (2013).

The stability of the cathode has been tested, but there is not sufficient experimental data for this specific electrode to estimate its lifetime at a larger scale. In this model we assume the lifetime to be 5000 hours, being the average stack lifetime of polymer electrolyte membrane fuel cells, which have considerably shorter lifespan than alkaline systems (Myers et al. 2012). The inventory for the electrolyser stack is shown in Table B1.

Table B1. Inventory for the electrolyser stack	
Parameter	Amount
Functional unit output	
Electrolyser stack [unit]	1
Material requirements	
Assembled electrolyser [unit]	15429
Infrastructure requirements	
Occupation, industrial area [m <sup>2</sup> a]	2609.6
Transformation, from unknown [m <sup>2</sup> ]	347.9
Transformation, to industrial area [m <sup>2</sup> ]	347.9

### B1.1 Manufacture of assembled electrolyser

The build of the flow cell electrolyser is shown in Wang *et al.* (2020) and schematised in Li *et al.* (2020) The prepared cathode electrode, gas diffusion layer (GDL), anion exchange membrane (AEM), and Ni foam anode are clamped and assembled using polytetrafluoroethylene (PTFE) spacers. The inventories for the mentioned elements are given in later subsections. The frame of the cell consists of compression plates and bolts holding together the cell assembly. The frame is assumed to be low-alloy steel plates compressed with 8, ¼ inch bolts, as manufactured in Li & Oloman (2005) for a conservative approach. However, using 3D printed cheaper thermoplastics, such as polylactic acid in Hudkins *et al.* (2016) would result in cheaper manufacturing with



potentially lower environmental impacts. The lifetime of the frame is assumed 20 years, being possible to replace the electrolyser stack at the end of its lifetime (60,000 hours) and keep using the same frame.

The material requirements follow the necessary components normalised to the lifetime of the frame. The PTFE spacers are estimated to double the dimension of the longer side of the membrane according the schematic of the flow cell in Wang *et al.* (2020) and Li *et al.* (2020). The PTFE spacer thickness is assumed to be 1.5 mm as the average thickness of spacers commercialised by Klinger Australia (n.d.). The area of the plates are the sum of the membrane and the gasket. The depth of the cell (3.0 cm) and thickness of the steel plates (0.3 cm) are taken from Hudkins *et al.* (2016). Bolts are assumed ¼” x 1 ¼” steel, with one in each corner of the frame.

The energy requirements for the frame are embodied by the steel manufacturing process. For the assembly, the electricity per square meter defined by Duclos *et al.* (2017) is used. Transport requirements are neglected since assembly is assumed to happen on-site. Infrastructure requirements are not allocated to this inventory since they are aggregated with the adsorption and distillation system. Waste and emissions are associated with the end of life disposal of each component considered in their corresponding inventory, with the exception of the disposal of the frame that is specified here.

As previously mentioned, the electrolyser was scaled by increasing the size of the electrode area to 2 m<sup>2</sup>. The side of the spacers in the scaled-up electrolyser was assumed to be 1.2 times the length of the electrode rather than double as in the original lab-scale design. This was assumed as an improved design efficiency, using a relatively lower amount of PTFE for the gasket and steel for the frame. The thickness of the frame and electrolyser was kept identical. The detailed inventory is shown in Table B2.

Table B2. Inventory for the assembled electrolyser

Parameter	Amount
Functional unit output	
Assembled electrolyser [unit]	1
Material requirements	
PTFE [kg]	0.54
Low-alloyed steel, frame [kg]	117.54
Low-alloyed steel, bolts [kg]	0.78
N-C/Cu electrode [m <sup>2</sup> ]	64.00
Ni foam [kg]	1.85
Anion exchange membrane [m <sup>2</sup> ]	5.33
Gas diffusion layer [m <sup>2</sup> ]	5.33
KOH electrolyte 1M [kg]	1680.00
Steel product manufacturing [kg]	117.54
Energy and processing requirements	
Assembly, electricity [MJ]	32.03
Waste and emissions	
Disposal of steel to landfill [kg]	118.32
Plastics, mixture, to sanitary landfill	0.54

## B1.2 Manufacture of N-C/Cu electrode

The N-C/Cu electrode was synthesised by sputtering a 200nm layer of copper nanoparticles as catalyst onto a PTFE membrane, followed by a 50nm layer of nitrogen-doped carbon (N-C) using a magnetron sputtering system. The specific nitrogen content of the N-C layer is 34%.

The material requirements were calculated from the experimental procedure assuming stoichiometric quantities. The PTFE membrane used in the catalyst synthesis was purchased from Beijing Zhongxingweiye Instrument Co., Ltd. This product has a specified thickness range of 198.1 – 269.2  $\mu\text{m}$ . In this inventory, the average thickness was used to calculate the volume of PTFE needed. The mass of PTFE required was calculated by taking as base the density of the PTFE membrane commercialised by Microlab Scientific (n.d.) with a weight of 30 g/m<sup>2</sup> and a thickness of 122  $\mu\text{m}$ .

Since no specifications are given, the associated energy requirements of a sputtering process of indium tin oxide for liquid crystal display inecoinvent (modified

with AusLCI data) and the transport of its targets were used as a proxy, adapting the quantity to the specific dimensions of each layer. The process for copper layering in ecoinvent specifies a 50% efficiency of the targets, so material requirements were increased to consider this loss. The infrastructure requirements are standard from ecoinvent guidelines. Due to lack of data, no direct material losses or emissions are associated to this process other than the disposal and recycling of material lost and waste heat. The disposal of a catalyst for ethylene dichloride (EDC) production is used as a proxy for the end of life of this catalyst as hazardous waste incineration. The detailed inventory can be found in Table B3.

Table B3. Inventory for the manufacture of N-C/Cu electrode

Parameter	Amount
Functional unit output	
N-C/Cu electrode [m <sup>2</sup> ]	1
Material requirements	
PTFE [kg]	0.057
Copper, primary [kg]	0.004
Nitrogen, at plant [kg]	0.0005
Argon, at plant [kg]	0.0022
Graphite, battery grade, at plant [kg]	0.0008
Energy and processing requirements	
Electricity for sputtering [kWh]	7.319
Transport requirements	
Freight aircraft transport [tkm]	0.0090
Lorry >16t [tkm]	0.0002
Infrastructure requirements	
Facilities for production [kg]	1.47E-04
Chemical plant [unit]	4.00E-10
Waste and emissions	
Disposal of copper [kg]	0.0019
Carbon, as graphite [kg]	0.0004
Nitrogen [kg]	0.0002
Argon [kg]	0.0011
Disposal of catalyst (proxy with catalyst for EDC production) [kg]	0.0600
Waste heat [MJ]	26.35

### B1.3 Manufacture of Ni foam catalyst

Nickel foam is a porous material with high electronic conductivity and surface area, typically manufactured by electrodeposition or chemical vapour deposition of nickel ions as coating on a polymer (Chaudhari et al. 2017). The specific Ni foam used as anode catalyst in Wang *et al.* (2020) is commercially produced by MTI Corporation (product number: Eq-bcnf-16m). Given the manufacturing details of this Ni foam are not publicly available, the electrodeposition of nickel ions in the form of  $\text{NiSO}_4$  on polyurethane foam from Liu and Liang (2000) is assumed.

The material requirements were calculated from the information available for this product (namely, surface density of  $346 \text{ g/cm}^2$  and a thickness of 1.6 mm). The energy, transport, and infrastructure requirements and emissions are based on the LCA of Ni metal hydride electrode substrate in batteries of electric vehicles by Majeau-Bettez *et al.* (2011). The disposal of nickel at its end of life is approximated using the AusLCI process Disposal of copper with 0% water to municipal incineration. The detailed inventory is shown in Table B4.

Table B4. Inventory for the manufacture of Ni foam

Parameter	Amount
Functional unit output	
Ni foam, at plant [kg]	1
Material requirements	
Nickel, 99.5%, GLO (proxy for electroplated NiSO <sub>4</sub> ) [kg]	1
Polyurethane, flexible foam [kg]	0.028
Energy and processing requirements	
Heat, unspecific, in chemical plant (burn-off polyurethane) [MJ]	0.078
Heat, unspecific, in chemical plant (sinter) [MJ]	1.5
Transport requirements	
Freight rail transport [tkm]	0.61
Lorry >16t [tkm]	0.10
Infrastructure requirements	
Chemical plant [unit]	4.0E-10
Waste and emissions	
Waste polyurethane, open burning (proxy for combustion) [kg]	0.028
Waste heat [MJ]	1.578
Disposal of nickel to incineration [kg]	1

## B1.4 Manufacture of anion exchange membrane

Anion exchange membranes (AEM) are generally composed of a polymer as main structure with cationic sites that allow the pass of hydroxide ions and other anions between anode and cathode (Pan et al. 2018). The specific AEM used in the flow cell electrolyser of Wang *et al.* (2020) is the commercial product Fumasep FAB-PK-130 (product code: 5041636) manufactured by Fuel Cell Store. Although the Technical Sheet for this product has a comprehensive characterisation of its conductivity and strength properties, there is not sufficient information on its composition or manufacture process. Therefore, the synthesis of an imidazolium functionalised polysulfone AEM as designed by Zhang *et al.* (2011) was used as proxy, since their membrane has comparable conductive properties.

The material requirements were calculated based on the experiment of Zhang *et al.* (2011). The energy requirements were calculated by the thermodynamic heating and boil-off of the solvents and unreacted chemicals in the experiment, neglecting the

power needed for the stirring involved. As in Simons and Bauer (2015), the energy requirements and waste/emissions of extrusion to plastic films were added as a proxy for its industrial manufacture, relating the needed fraction according to the weight of the membrane as plastic. The weight of the membrane was determined as 3.34 mg/cm<sup>2</sup> according to the calculated molecular weight of the membrane, the stoichiometry of the reactions, and the area of the membrane produced. Transport and infrastructure requirements are standard from ecoinvent guidelines. No pre-treatment losses were considered. The waste and emissions are carried from the extrusion process, except the disposal of the membrane that is taken from the ecoinvent process Spent anion exchange resin from potable water production as a proxy. The detailed inventory is presented in Table B5.

Table B5. Inventory for the manufacture of the anion exchange membrane

Parameter	Amount
Functional unit output	
Anion exchange membrane, at plant [m <sup>2</sup> ]	1
Material requirements	
Polysulfone [kg]	0.021
Chloromethylmethylether (CMME) [kg]	0.035
N-N Dimethylacetamide (DMAc) [kg]	0.468
Imidazole [kg]	0.007
Methanol [kg]	0.016
NaOH [kg]	0.003
Water, completely softened [kg]	0.171
Water, cooling, unspecified [m <sup>3</sup> ]	0.0015
Energy and processing requirements	
Heat, unspecific, at chemical plant (boil-off solvents) [MJ]	0.305
Electricity [kWh]	0.022
Heat, natural gas [MJ]	0.020
Heat, other than natural gas [MJ]	0.007
Steam in chemical industry [kg]	0.002
Transport requirements	
Freight rail transport [tkm]	0.330
Lorry >16t [tkm]	0.055
Infrastructure requirements	
Chemical plant [unit]	1.34E-11
Waste and emissions	
Water, emissions to air [m <sup>3</sup> ]	0.0006
Water, emissions to water [m <sup>3</sup> ]	0.0009
Waste mixed plastics, inefficiencies [kg]	0.0008
Disposal of anion exchange membrane to incineration [kg]	0.0335

## B1.5 Manufacture of the gas diffusion layer

Wang *et al.* (2020) used a carbon paper (CP) gas diffusion layer (GDL) with a microporous layer (MPL) manufactured by Fuel Cell Store under the product name of Freudenberg H14CP. CP is composed of hot pressed and carbonised carbon fibres with phenolic resin, and the MPL is usually composed of carbon black powder and PTFE (Duclos et al. 2017).

The material requirements of the CP were based on Hung *et al.* (2015), with a concentration of phenolic resin of 15% wt. The material requirements of the MPL were

based on Park *et al.* (2008), with a carbon loading of 2 mg cm<sup>-2</sup> and PTFE content of 20% wt. The carbon fibre weight was modified to match the area weight of 100 g·m<sup>-2</sup> specified for Freudenberg H14CP in its technical datasheet. The organic solvents used in manufacture were not modelled. No pre-treatment losses were considered.

The energy requirements for the treatment and manufacture of the GDL are based on the work of Simons and Bauer (2015) and Evangelisti *et al.* (2017), using a thermoforming calendaring process as proxy.

Transport requirements and infrastructure are identical to the inventory for the AEM since they are assumed to come from the same source. The disposal of the GDL is associated with waste of mixed plastics in landfill with approximately 15% water content. The detailed inventory is shown in Table B6.

Table B6. Inventory for the manufacture of the gas diffusion layer	
Parameter	Amount
Functional unit output	
Gas diffusion layer, at plant [m <sup>2</sup> ]	1
Material requirements	
Carbon fibre [kg]	0.06
Phenolic resin [kg]	0.015
Carbon black [kg]	0.02
PTFE [kg]	0.005
Energy and processing requirements	
Heat, steam [MJ]	0.085
Heat, natural gas, at industrial furnace >100kW [MJ]	0.169
Electricity, grid [MJ]	3.58
Heat, heavy fuel oil, at industrial furnace 1MW [MJ]	0.222
Transport requirements	
Freight rail transport [tkm]	0.06
Lorry >16t [tkm]	0.01
Infrastructure requirements	
Chemical plant [unit]	4.0E-11
Waste and emissions	
Waste mixed plastics [kg]	0.012

The process for carbon fibre production was extracted from the Data on Production of Chemicals created for the EU Product Environmental Footprint (Wernet et al. 2017)



and shown in Table B7. There are no assigned transport requirements since the process is assumed to happen on-site along with the GDL.

Table B7. Inventory for the production of carbon fibre

Parameter	Amount
Functional unit output	
Carbon fibre production, AU tech mix, at plant [kg]	1
Material requirements	
Argon, liquid [kg]	0.01
Lubricating oil [kg]	0.0002
water, completely softened, from decarbonised water, at user [kg]	0.057
water, decarbonised, at user [kg]	1.902
Acrylic fibre [kg]	2.08
Energy and processing requirements	
Heat, district or industrial, natural gas [MJ]	15.37
Natural gas, at consumer [kg]	0.37
Electricity, grid [kWh]	20.20
Heat, unspecific [MJ]	45.58
Infrastructure requirements	
Chemical plant [unit]	4.00E-10
Gas power plant [unit]	5.29E-10
Heat power cogeneration unit 1MW, electric+heat [unit]	3.28E-09
Heat power cogeneration unit 1MW, electric only [unit]	3.28E-09
Heat power cogeneration unit 1MW, heat only [unit]	3.28E-09
Heat power cogeneration unit 200kW, electric+heat [unit]	8.01E-09
Heat power cogeneration unit 200kW, electric only [unit]	8.01E-09
Heat power cogeneration unit 200kW, heat only [unit]	8.01E-09
Heat power cogeneration unit 500kW, electric+heat [unit]	2.72E-09
Heat power cogeneration unit 500kW, electric only [unit]	2.72E-09
Heat power cogeneration unit 500kW, heat only [unit]	2.72E-09
Industrial furnace, natural gas [unit]	3.84E-09
Waste and emissions	
Residue from cooling tower [kg]	9.51E-06
Waste mineral oil [kg]	0.0002

The acrylic fibre production process was extracted directly from the LCA by Yacout *et al.* (2016) and shown in Table B8. There are no assigned transport requirements since the process is assumed to happen on-site along with the carbon fibre and GDL.

Table B8. Inventory for the production of acrylic fibre

Parameter	Amount
Functional unit output	
Acrylic fibre [kg]	1
Material requirements	
Acrylonitrile [kg]	0.91
Vinyl acetate [kg]	0.09
Sodium chlorate [kg]	0.006
Sodium metabisulfite [kg]	0.018
Sulfuric acid [kg]	0.0003
Sodium hydroxide (50%) [kg]	0.019
Titanium dioxide [kg]	0.0042
Sodium sulfate [kg]	0.007
Nitric acid [kg]	0.0024
Demineralized water [kg]	143.57
Energy and processing requirements	
Electricity, grid [kWh]	1.32
Steam [kg]	9.8
Infrastructure requirements	
Chemical plant [unit]	4.0E-10
Waste and emissions	
Waste effluent [m <sup>3</sup> ]	0.069
Hazardous waste from process [kg]	0.001
Chemical sludge [kg]	0.0012
Reused mixed plastics containers [kg]	0.0010

## B1.6 Manufacture of electrolyte

The electrolyte used in the flow cell electrolyser is 1 M potassium hydroxide (KOH). The material requirements are a simple calculation of its components. Energy requirements for stirring are neglected. The deionization of water and the salt dissolution were assumed to be performed on-site at the electrolyser plant, thus no infrastructure requirements were assigned to this process. The waste and emissions are 95% of the water disposed as waste water and waste treatment of sludge, using the disposal of sludge from NaCl electrolysis as proxy. The inventory is shown in Table B9.

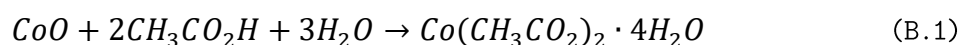
Table B9. Inventory for the production of KOH 1M electrolyte

Parameter	Amount
Functional unit output	
KOH electrolyte 1M [kg]	1
Material requirements	
Potassium hydroxide [kg]	0.05
Water, completely softened [kg]	0.95
Transport requirements	
Freight rail transport [tkm]	0.60
Lorry >16t [tkm]	0.10
Waste and emissions	
Waste treatment, sludge from electrolysis [kg]	0.06
Water [kg]	0.94

## B1.7 Manufacture of Fe-Co composite film on carbon fibre paper electrode

This inventory was compiled as a substitute anode for the electrolyser. This inventory is based on the work of Liu *et al.* (2017), where the authors prepared a Fe-Co composite film electrodeposited on a carbon fibre paper (CFP) to be used as an electrode with a high oxygen evolution reaction (OER) performance in KOH solutions, such as the one used in this model. The material requirements were calculated from the experimental section of their publication, using iron (III) sulfate and cobalt (II) acetate tetrahydrate in an acetate buffer solution (pH=5.0).

Since the LCI databases lack some of the specific chemicals employed, the inventory was created using stoichiometric quantities of the precursors in the synthesis of these chemicals. Acetic acid and sodium hydroxide are accounted to synthesise sodium acetate in the buffer solution. Water and acetic acid with gray cobalt (CoO) are used to synthesise cobalt (II) acetate tetrahydrate as in the following reaction:



Gray cobalt production is based on the ecoinvent process for global cobalt production, but the carbon monoxide, hydrogen, and heat required to reduce CoO to metallic Co were removed. The specific CFP used by Liu *et al.* (2017) is product HCP030 from Shanghai Hesun Electric Co., Ltd, which has a thickness of 0.3 mm and a density of 0.78 g/cm<sup>3</sup>. The carbon fibre inventory created in this assessment is used to account for the required mass.

The energy, transport, and infrastructure requirements are derived in the same way as for the Ni foam electrode, which are based on the inventory by Majeau-Bettez *et al.* (2011), accounting for a mass density of 0.246 kg/m<sup>2</sup> (considering the mass of carbon fibre and the loading mass of the catalyst). The disposal of the electrode at its end of life is approximated using the AusLCI process Iron and steel hydrometallurgical processing in Li-ion batteries. The detailed inventory is shown in Table B10.

Table B10. Manufacture of Fe-Co composite film electrode	
Parameter	Amount
Functional unit output	
Fe-Co composite film electrode, at plant [m <sup>2</sup> ]	1
Material requirements	
Iron sulfate [kg]	0.007
Gray cobalt (CoO) [kg]	0.002
Acetic acid [kg]	3.605
Water, completely softened [kg]	0.001
NaOH [kg]	1.616
Carbon fibre [kg]	0.234
Energy and processing requirements	
Heat, unspecific, in chemical plant (sinter) [MJ]	1.5
Transport requirements	
Freight rail transport [tkm]	0.150
Lorry >16t [tkm]	0.025
Infrastructure requirements	
Chemical plant [unit]	9.84E-11
Waste and emissions	
Disposal and processing of iron from batteries [kg]	0.246

## B2. Direct air capture system

The direct air capture (DAC) process modelled is based on the process described by Keith *et al.* (2018) and analysed by Liu *et al.* (2020). While it is still a design, all performance estimates are based on commercially available equipment, a proven process at a smaller-scale Carbon Engineering pilot plant, iterative prototypes developed by Royal HaskoningDHV, and comprehensive techno-economic analyses (Keith et al. 2018). Actual scale-up could still bring improvements or negative changes to the performance estimates.

The material requirements for the DAC plant are calculated from the initial chemicals needed to start the process in the plant. The land area associated with the plant is calculated from the quoted dimensions in an earlier publication by Holmes and Keith (2012): 0.016 km<sup>2</sup>/Mt CO<sub>2</sub>-year. However, the actual land use would be higher given those are only corresponding to the packings (Viebahn et al. 2019). Therefore, a two-fold increase in total land use was assumed. The cryogenic air separation unit in the original plant is not considered in the assessment because, unlike the oxy-fired calciner, the electric calciner does not need oxygen. The only known data for wastes and emissions are the embodied emissions in the construction and decommissioning of the plant quantified in Liu *et al.* (2020) as direct CO<sub>2</sub> emissions in the inventory. The emissions of the equipment not needed in this model were excluded. The inventory for the DAC plant is presented in Table B11.

Table B11. Inventory for the Direct Air Capture plant

Parameter	Amount
Functional unit output	
DAC plant [unit]	1
Material requirements	
Potassium hydroxide [kg]	9.96E+05
Potassium carbonate [kg]	1.23E+06
Water, completely softened [kg]	1.78E+07
Calcium hydroxide (KOH as proxy) [kg]	1.10E+05
Infrastructure requirements	
Occupation, construction site [m <sup>2</sup> a]	48,980
Occupation, industrial area [m <sup>2</sup> a]	979,592
Transformation, from unknown [m <sup>2</sup> ]	48,980
Transformation, to industrial area [m <sup>2</sup> ]	48,980
Waste and emissions	
CO <sub>2</sub> -e emissions (construction & decommissioning) [kg]	2.13E+08

The inventory for the process of captured CO<sub>2</sub> as product was developed considering all make-up flows and losses. The inefficiencies in the captured and supplied CO<sub>2</sub> are considered as emissions back to the atmosphere. The plant design includes compression and clean-up of the product CO<sub>2</sub> from atmospheric pressure up to 150 bar. Although the ECCR operates at atmospheric pressure and would not need such high compression, it would still need to be scrubbed and dehydrated. Therefore, half of the power requirements associated with this subprocess are maintained in the model. This assumption is very conservative as it may overestimate the electricity required to provide the captured CO<sub>2</sub>. Its inventory is presented in Table B12.

Table B12. Inventory of captured CO<sub>2</sub> from Direct Air Capture

Parameter	Amount
Functional unit output	
Captured CO <sub>2</sub> , DAC [kg]	1
Material requirements	
Carbon dioxide, in air [kg]	1.37
Potassium hydroxide [kg]	2.15E-04
Water, completely softened [kg]	4.162
Calcium carbonate [kg]	0.027
Energy and processing requirements	
Electricity [kWh]	0.244
Infrastructure requirements	
DAC plant [unit]	4.47E-11
Waste and emissions	
Carbon dioxide, air [kg]	0.37
Potassium hydroxide, air (NaOH as proxy) [kg]	2.15E-04
Calcium carbonate, waterborne disposal [kg]	0.027

### B3. Adsorption system

The adsorbent selected for the adsorption bed is activated carbon (AC) (type BPL, 6/16 mesh, manufactured by the Pittsburgh Chemical Company) owing to the results of Zandvoort *et al.* (2020) in comparing cation zeolites and AC for various C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub> ratios. The design of the bed (namely, length/diameter ratio and thickness) is based on the experiments of Casas *et al.* (2012), scaled to match the required volume.

The adsorption system comprises two packed beds and the required total AC adsorbent in the lifetime of the system. The lifetime of each packed adsorption bed was assumed 20 years and of AC, 5 years, as estimated in Beccali *et al.* (2014). The material requirements are assumed to be stainless steel (Grade 304) for the case of the packed bed and plates. Energy requirements are included in the material extraction and manufacturing processes, and an estimated amount of electricity for welding based on the design of the bed.

The infrastructure requirements involve the factory, equipment, and land use needed to house the entire system. In order to estimate these values, the requirements for the ecoinvent process for an *Air separation facility* were used as a base, with the size scaled to the specific output of the adsorption system. The transport requirements to bring all the materials to a remote location were based on the distance from Brisbane to Dalby, first through freight rail to Toowoomba and then on a >32t lorry to Dalby. The wastes and emissions are the disposal of AC and steel at the end of lifetime of the AC and the complete facilities. The detailed inventory is shown in Table B13.



Table B13. Inventory for the adsorption system

Parameter	Amount
Functional unit output	
Adsorption system [unit]	1
Material requirements	
Activated carbon [t]	518.72
Stainless steel [t]	33.45
Stainless steel manufacturing [t]	33.45
Infrastructure requirements	
Occupation, construction site [m <sup>2</sup> a]	329
Occupation, industrial area [m <sup>2</sup> a]	6577
Transformation, from unknown [m <sup>2</sup> ]	329
Transformation, to industrial area [m <sup>2</sup> ]	329
Aluminium, wrought alloy [kg]	3288
Chemical factory [kg]	29595
Energy and processing requirements	
Electricity, welding [kWh]	0.47
Transport requirements	
Freight rail transport [tkm]	55217
Lorry >32t [tkm]	44174
Waste and emissions	
Carbon (disposal of AC) [t]	518.72
Disposal of steel to landfill [t]	33.45
Decommissioned chemical production facilities [kg]	29595

## B4. Ethanol production by ECCR system

This process comprises the entire production of 1kg of ethanol at 95% m/m through the electrocatalytic reduction of captured CO<sub>2</sub> obtained through direct air capture (DAC), and subsequent separation in the distillation system. Ethylene is a co-product separated through the adsorption system. The co-production is solved through system expansion by substitution, modelling ethylene production through ethane cracking, being the traditional benchmark.

The specific process used for ethylene production is an AusLCI inventory created on data provided by Qenos for their Botany Bay plant in New South Wales (NSW). The effect of the credit of the ethylene co-production is significant in the associated impact of the system. The validity for this particular assessment stands from a geographic perspective, as it is the current method to produce ethylene in an olefines production plant in the area of study. An LCA with a wider scope could incorporate the effect of cleaner energy or innovative processes for ethylene production. This may have an effect in the ultimate environmental impact of the proposed system.

The material requirements include the captured CO<sub>2</sub> (with its associated emissions and energy requirements), extra water for the electrolysis reaction and to maintain a constant volume of electrolyte, and the infrastructure requirements for the electrolyser stack, adsorption system, and distillation system. Make-up cooling water is required while the blowdown of the cooling tower is sent to wastewater treatment. The energy requirements include all electricity needed for each of the three systems. Details of their calculation can be found in their corresponding section. The thermal energy required is provided by an electric boiler with an assumed 95% efficiency. The total electricity requirement is met by medium voltage electricity from the different electricity grid scenarios.

All other transport and infrastructure requirements and wastes are implicit in the inventory of the subprocesses or materials. The infrastructure requirements for the distillation system use theecoinvent process *Ethanol fermentation plant* as a proxy, assuming 60% of the entire plant to consider only the distillation columns needed. This assumption may be conservative considering fermenters usually involve the highest equipment and land component of the plant. The detailed inventory is presented in Table B14.

Table B14. Inventory of ethanol production via the ECCR system	
Parameter	Amount
Functional unit output	
Ethanol production, by ECCR plant [kg]	1
Co-production output (avoided products)	
Ethylene, at plant [kg]	0.416
Material requirements	
Captured CO <sub>2</sub> , DAC [kg]	3.123
Water, completely softened [kg]	2.028
Cooling water [m <sup>3</sup> ]	8.51E-04
Infrastructure requirements	
ECCR stack [unit]	7.91E-10
Adsorption system [unit]	7.91E-10
Distillation system [unit]	5.00E-10
Energy and processing requirements	
Electricity, ethylene separation (adsorption system) [kWh]	0.455
Electricity, compression (pre-adsorption recirculation) [kWh]	0.555
Heat, steam (distillation system) [MJ]	3.416
Electricity, cooling water (distillation system) [kWh]	0.003
Electricity, air cooling (distillation system) [kWh]	0.004
Electricity, compressors + pumps (distillation system) [kWh]	0.207
Electricity (electrolyser) [kWh]	27.066
Electricity (electrolyte pumps) [kWh]	0.879
Waste and emissions	
Water to wastewater treatment [m <sup>3</sup> ]	1.70E-04

## B5. Ethanol production by the bioethanol benchmark system

The largest producer of bioethanol in Queensland is Dalby Biorefinery, producing approximately 76 ML/a of bioethanol by the fermentation of red sorghum grain (Farrell & Santella 2019). The bioethanol benchmark process in the LCA is based on a plant with the same size, output, and feedstock.

The AusLCI database already has an allocated process for ethanol production based on data collected and estimated for a plant similar to Dalby Biorefinery. The economic allocation for ethanol is 75.3% and includes a carbon correction to satisfy the carbon balance of the DDGS. Modifications were done to adjust the performance to specifications in newer publications (Queensland Government 2017) and personal communication (Sharp 2020). Particular subprocesses were also adjusted to more closely reflect the geography of Dalby Biorefinery. Finally, other material requirements and wastes were complemented from ecoinvent processes for bioethanol production from wheat and sweet sorghum, adapting to the specific process and composition of red sorghum. Sorghum as a crop is modelled with high resolution in the AusLCI database, as a special inventory developed by CSIRO, the Department of Primary Industries NSW and Lifecycles for the AusLCI database (Australian Life Cycle Assessment Society 2020).

The conversion of sorghum to ethanol was modelled as 2.5 kg sorghum/kg ethanol, as specified in a plant report (Queensland Government 2017). Using the estimate in the AusLCI database process of 0.282 kg DDGS/kg sorghum, the yield of DDGS is 0.892 kg DDGS/kg ethanol. Water requirements were based on the AusLCI and ecoinvent processes, and they are consistent with the range provided by first-hand information and specified in the same report (Queensland Government 2017). Yeast is

not included as a material requirement since it is assumed to be recovered and propagated for consecutive fermentations. Material and energy requirements and waste treatments associated with yeast harvesting and propagation are not considered.

The energy requirements are based on the energy consumption specified in the plant report (Queensland Government 2017), differentiated between thermal and electrical energy according to the proportional spread in the AusLCI process. The thermal and electric energy requirements specific to dehydration (1 MJ and 0.0088 kWh per kg of ethanol, respectively) were removed in order to produce the functional unit at the same purity (95% m/m).

The infrastructure requirements are the ethanol fermentation plant itself, based on the total production of ethanol by the plant in the estimated 20 years of operational lifetime. The land use and occupation was calculated by measuring the area around Dalby Biorefinery in satellite photography (Google n.d.). No construction or land transformation was considered. Transport requirements are based on the transport of sorghum from farm to plant and on the transport of natural gas in a pipeline to Dalby Biorefinery. Dalby uses a natural gas steam boiler to provide its heating requirements. The gas is obtained via the Dalby Gas Pipeline, an 8.9 km connection from the Dalby Compressor Station in the 438 km Roma to Brisbane gas pipeline (United Petroleum n.d.). Only half of the distance of the main gas pipeline is considered, given that the Dalby Gas Pipeline is roughly at the middle of it. CO<sub>2</sub> emissions represent only the stoichiometric emission of biogenic CO<sub>2</sub>: two moles of ethanol and two of CO<sub>2</sub> per mole of glucose. All other requirements and wastes are based on theecoinvent and AusLCI referenced processes. The unallocated inventory is shown in Table B15.

Table B15. Inventory of bioethanol production via sorghum fermentation

Parameter	Amount
Functional unit output	
Ethanol process from sorghum, QLD [kg]	1
Material requirements	
Sorghum grain, Western Downs and NW slopes and plains [kg]	1.055
Sorghum grain, northern zone NSW [kg]	1.055
Sorghum grain, Darling Downs, QLD [kg]	1.055
Lubricating oil [kg]	2.31E-04
Water, Darling Downs [kg]	7.296
Water, completely softened [kg]	0.015
Chlorine, liquid [kg]	6.43E-06
Sodium chloride, powder [kg]	8.03E-05
Sulfuric acid [kg]	0.027
Energy and processing requirements	
Heat, natural gas, at industrial furnace [MJ]	9.482
Electricity, QLD [MJ]	0.334
Infrastructure requirements	
Occupation, industrial area [m2a]	0.087
Ethanol fermentation plant [unit]	8.33E-10
Transport requirements	
Truck, 40t [tkm]	0.633
Pipeline, natural gas [tkm]	0.036
Waste and emissions	
Carbon dioxide, biogenic [kg]	0.955
Disposal, solid waste [kg]	6.43E-05
Disposal, used mineral oil [kg]	6.43E-05
Water to wastewater treatment [m <sup>3</sup> ]	1.54E-05

## B6. High and medium voltage electricity

The generation of high voltage and medium voltage electricity was modelled taking the corresponding AusLCI process as base, changing the electricity grid mix for each scenario. All emissions, infrastructure, and energy losses are considered. The inventory of high voltage generation and medium voltage is found in Table B16 and B17, respectively.

Table B16. Inventory for high voltage electricity generation

Parameter	Amount
Functional unit output	
Electricity, high voltage (High, Mid, Low) [kWh]	1
Energy and processing requirements	
Electricity grid mix (High, Mid, Low) [kWh]	1.045
Infrastructure requirements	
Transmission network, high voltage [km]	8.44E-09
Transmission network, long distance [km]	3.17E-10
Waste and emissions	
Ozone [kg]	4.50E-06
Dinitrogen monoxide [kg]	5.00E-06
Energy losses in electricity transmission [kWh]	0.045

Table B17. Inventory for medium voltage electricity generation

Parameter	Amount
Functional unit output	
Electricity, medium voltage (High, Mid, Low) [kWh]	1
Material requirements	
Sulfur hexafluoride, liquid [kg]	1.29E-07
Energy and processing requirements	
Electricity, high voltage (High, Mid, Low) [kWh]	1
Electricity, high voltage (High, Mid, Low) (voltage transformation loss) [kWh]	4.60E-03
Electricity, medium voltage (High, Mid, Low) (transmission loss) [kWh]	2.70E-03
Infrastructure requirements	
Transmission network, medium voltage [km]	1.86E-08
Waste and emissions	
Sulfur hexafluoride, to air [kg]	1.29E-07
Energy losses in electricity transmission [kWh]	7.30E-03

## B7. Distillation unit simulation stream table

Table B18. Full stream table of the converged distillation simulation model

Stream	1	2	3	4	5	6	7	8	9	10
Temperature [°C]	30.0	78.0	88.3	99.8	105.8	217.2	215.7	131.3	110.8	40.7
Pressure [bar]	2.6	1.9	1.2	1.1	1.2	3.1	3.1	3.1	2.8	2.1
Mass Vapor Fraction	0	0.001	0.005	1	0	1	1	1.000	0.075	0.038
Mass Liquid Fraction	1	0.999	0.995	0	1	0	0	0.000	0.925	0.962
Mass Enthalpy [J/kg]	-1.4E+07	-1.4E+07	-1.4E+07	-1.1E+07	-1.5E+07	-1.0E+07	-1.0E+07	-1.0E+07	-1.1E+07	-1.2E+07
Mass Flow [kg/s]	14.71	14.71	14.71	7.49	7.22	7.49	7.61	8.17	8.17	8.17
<i>Mass Fractions</i>										
H2O	0.755	0.755	0.756	0.664	0.865	0.664	0.654	0.669	0.669	0.669
CO2	0.001	0.002	0.003	0.040	0.000	0.040	0.041	0.039	0.039	0.039
H3O+	9.2E-10	3.3E-10	9.4E-11	0.0E+00	3.2E-12	0.0E+00	0.0E+00	1.1E-11	2.1E-07	6.1E-07
K+	0.036	0.036	0.036	0.000	0.073	0.000	0.000	0.000	0.000	0.000
OH-	6.4E-09	2.2E-07	1.2E-06	0.0E+00	2.8E-04	0.0E+00	0.0E+00	9.3E-14	2.9E-11	4.2E-13
HCO3-	0.056	0.055	0.051	0.000	0.006	0.000	0.000	0.000	0.000	0.000
CO3--	0.000	0.001	0.002	0.000	0.053	0.000	0.000	0.000	0.000	0.000
ETHANOL	0.152	0.152	0.152	0.296	0.003	0.296	0.305	0.292	0.292	0.292



Stream	11	12	13	14	15	16	17	18	19	20
Temperature [°C]	40.7	40.7	40.7	40.9	102.5	76.8	76.8	142.5	103.9	108.8
Pressure [bar]	2.1	2.1	2.1	5.0	4.3	1.1	1.1	3.1	2.6	3.1
Mass Vapor Fraction	1	0	0	0	0.001	0	1	1	0	0
Mass Liquid Fraction	0	1	1	1	0.999	1	0	0	1	1
Mass Enthalpy [J/kg]	-8.9E+06	-1.3E+07	-1.3E+07	-1.3E+07	-1.3E+07	-6.4E+06	-5.8E+06	-5.7E+06	-1.5E+07	-6.2E+06
Mass Flow [kg/s]	0.31	7.86	4.02	3.84	3.84	1.15	0.06	0.06	2.81	1.04
<i>Mass Fractions</i>										
H2O	0.013	0.695	0.695	0.695	0.695	0.050	0.019	0.019	0.975	0.050
CO2	0.973	0.003	0.003	0.003	0.003	0.000	0.167	0.167	0.000	0.000
H3O+	0.0E+00	6.3E-07	6.3E-07	6.3E-07	4.1E-07	5.9E-12	0.0E+00	0.0E+00	1.3E-08	3.7E-12
K+	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
OH-	0.0E+00	4.3E-13	4.3E-13	4.4E-13	1.3E-11	9.1E-17	0.0E+00	0.0E+00	1.2E-08	2.8E-16
HCO3-	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CO3--	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ETHANOL	0.014	0.303	0.303	0.303	0.303	0.950	0.814	0.814	0.025	0.950

Stream	21	22	23	24	25	26	27	28
Temperature [°C]	108.8	135.4	51.4	51.4	51.4	104.9	88.0	80.7
Pressure [bar]	3.1	3.3	2.6	3.5	2.6	2.6	1.9	1.9
Mass Vapor Fraction	1	0	0	0	0	0	0	0
Mass Liquid Fraction	0	1	1	1	1	1	1	1
Mass Enthalpy [J/kg]	-5.5E+06	-1.5E+07	-1.6E+07	-1.6E+07	-1.6E+07	-1.5E+07	-1.5E+07	-1.5E+07
Mass Flow [kg/s]	0.12	2.68	2.68	0.50	2.18	10.02	10.02	12.20
<i>Mass Fractions</i>								
H2O	0.021	0.975	0.975	0.975	0.975	0.895	0.896	0.910
CO2	0.089	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H3O+	0.0E+00	2.2E-08	4.1E-09	4.1E-09	4.1E-09	3.0E-12	2.7E-12	2.4E-12
K+	0.000	0.000	0.000	0.000	0.000	0.053	0.053	0.043
OH-	0.0E+00	1.9E-08	3.6E-09	3.6E-09	3.6E-09	2.9E-04	1.7E-04	1.3E-04
HCO3-	0.000	0.000	0.000	0.000	0.000	0.004	0.004	0.003
CO3--	0.000	0.000	0.000	0.000	0.000	0.038	0.038	0.031
ETHANOL	0.890	0.025	0.025	0.025	0.025	0.009	0.009	0.012

Stream	29	30	31	32
Temperature [°C]	30.0	30.0	92.5	50.0
Pressure [bar]	1.2	1.8	3.2	2.5
Mass Vapor Fraction	0	0.992	0	0
Mass Liquid Fraction	1	0.008	1	1
Mass Enthalpy [J/kg]	-1.5E+07	-9.0E+06	-6.3E+06	-6.4E+06
Mass Flow [kg/s]	12.20	0.31	2.19	2.19
<i>Mass Fractions</i>				
H2O	0.910	0.013	0.050	0.050
CO2	0.000	0.973	0.000	0.000
H3O+	1.4E-12	3.7E-09	4.8E-12	7.5E-12
K+	0.043	0.000	0.000	0.000
OH-	1.5E-05	1.0E-15	1.6E-16	2.7E-17
HCO3-	0.003	0.000	0.000	0.000
CO3--	0.032	0.000	0.000	0.000
ETHANOL	0.012	0.014	0.950	0.950

## B8. Theoretical energy requirements calculation

An Aspen simulation was constructed using a stoichiometric reactor and two component separators. CO<sub>2</sub> and water are used as input to the reactor and are completely converted to the relevant products of the electrolyser: ethanol, ethylene, hydrogen, and oxygen. Figure B1 illustrates the process flowchart. The yield to every product of the cathode was modelled according to their Faradaic efficiency: 53%, 38%, and 9% for ethanol, ethylene, and hydrogen, respectively. The first component splitter separates the oxygen of the products of the cathode. The second splitter separates the ethanol from the ethylene and hydrogen. The input stream of water is split to deliver the stoichiometric quantity for the reaction, while a fraction is bypassed to be mixed with the stream of ethanol at the end. This emulates the condition of the functional unit of the ECCR system, which is ethanol at 95% m/m.

Table B19 shows the energy requirements of every block. The basis of the stoichiometric calculation was the water used, at 100 kmol/h. An extra 2.9 kmol/h are accounted for mixing with the ethanol stream. The final stream of ethanol at 95% has a flowrate of 24.6 kmol/h or 1,053.0 kg/h. Given the product flowrate of ethanol in the ECCR system is 7900.46 kg/h, the energy requirements were scaled by 7.5. Hence, the total theoretical energy requirements of the scaled system are 109.8 MW. With respect to the real energy requirements of the ECCR system, the efficiency of the entire plant is 46%.

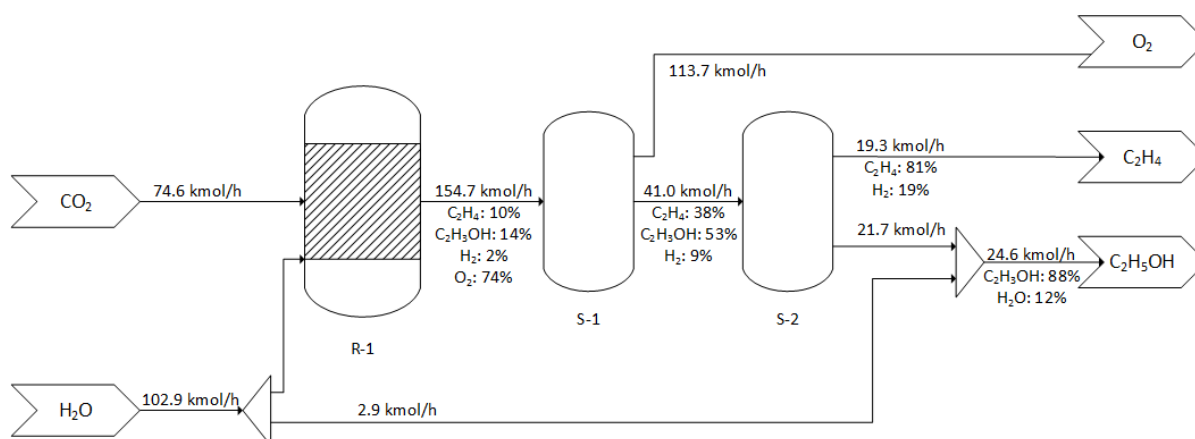


Figure B1. Process flowchart of theoretical conversion and separation. Composition percentages are mole fractions. The ethanol product is 95% m/m or 88% mol/mol

Table B19 Energy requirements of each block in theoretical process flowchart

Block	Energy requirement [MW]
Stoichiometric reactor R-1	14.819
Oxygen splitter S-1	-0.157
C2 splitter S-2	-0.026
<b>Total</b>	<b>14.636</b>

## B9. Additional plots

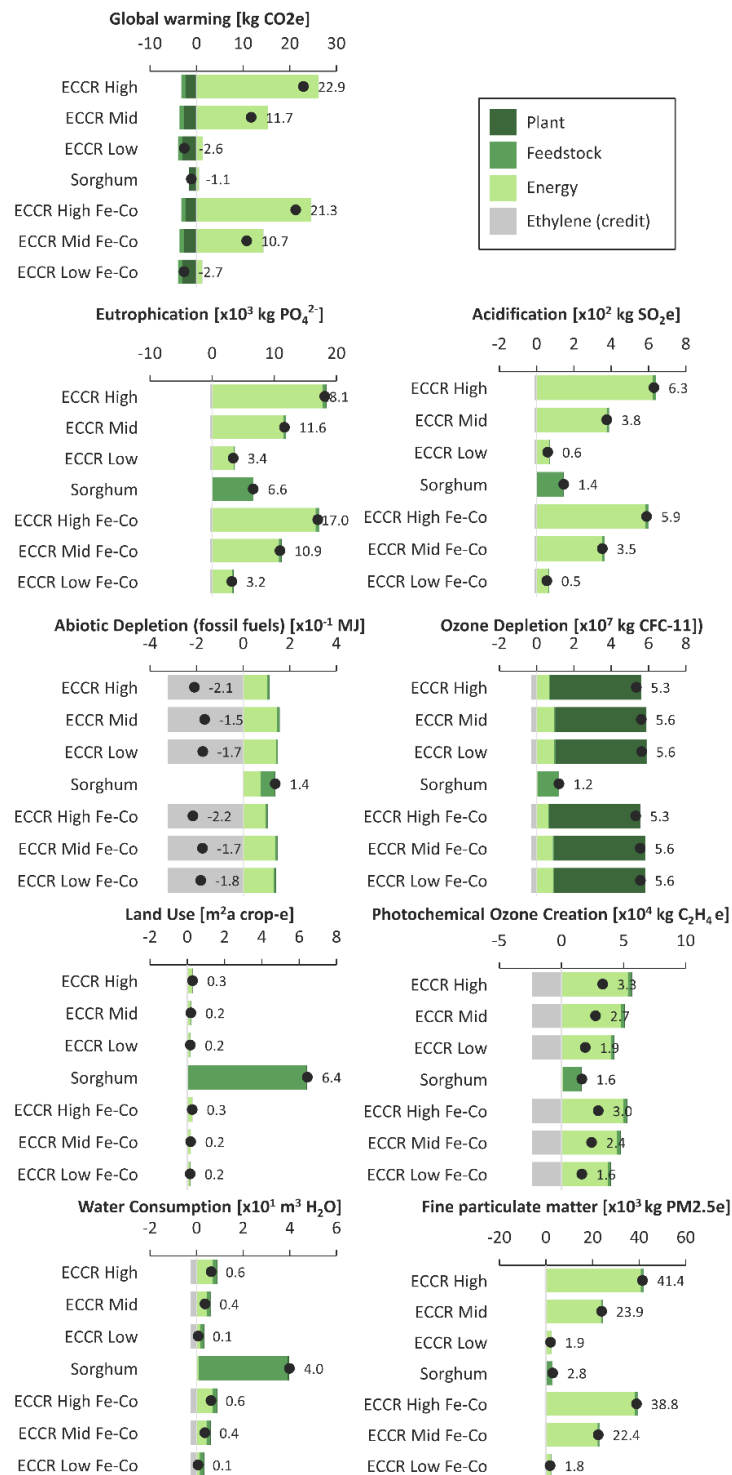


Figure B2. Potential environmental impacts in all categories for the electrocatalytic captured CO<sub>2</sub> reduction (ECCR) system, sorghum bioethanol, and the ECCR system with the Fe-Co anode substitute, using electricity from the three different scenarios (High, Mid, Low)

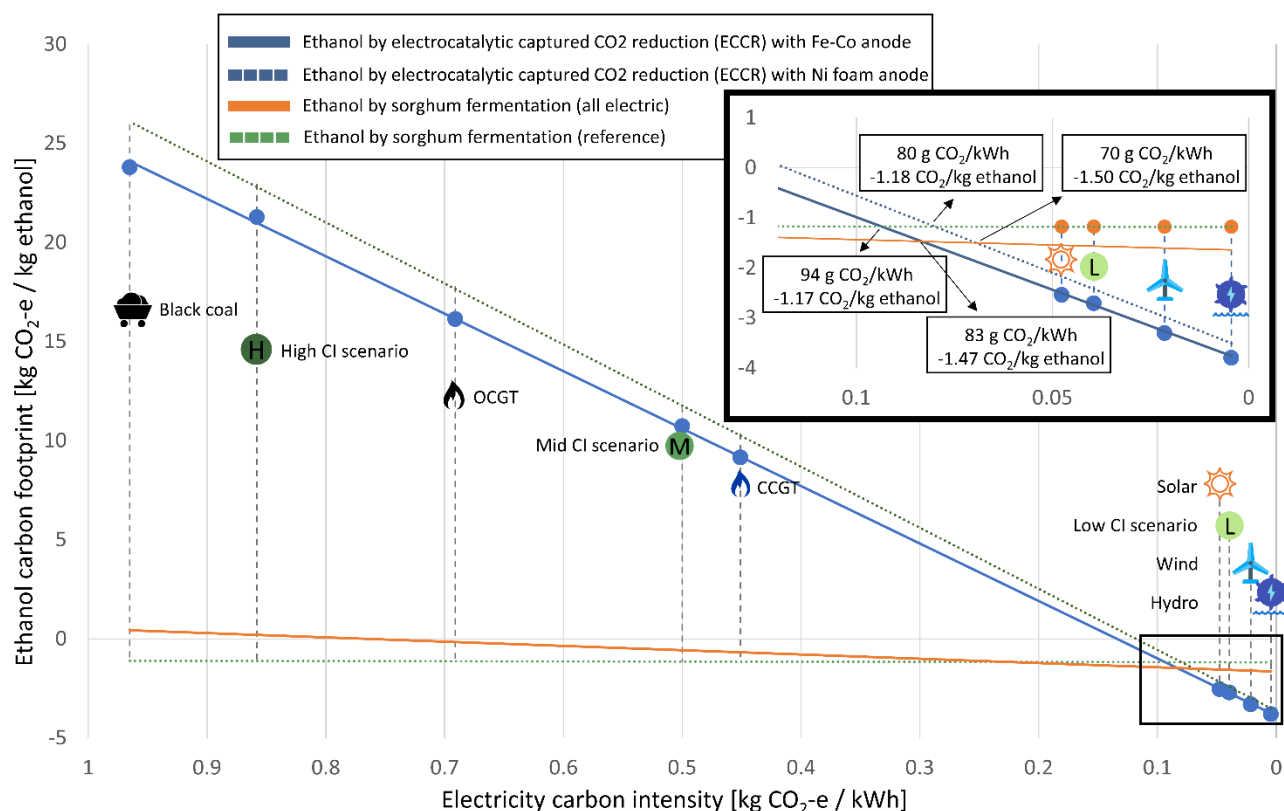


Figure B3. Carbon footprint of ethanol production by ECCR using a Fe-Co anode (continuous blue line) and a Ni foam anode (dotted blue line), and by sorghum using only electricity (orange continuous line) and by the reference sorghum process (dotted green line) with electricity of different sources and carbon intensity. Icons taken from open-source websites icons8.com and cleanpng.com