Advances in biorenewables-resource-waste systems and modelling

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Abstract

The transformation to a resource-circular bio-economy offers a mechanism to mitigate climate change and environmental degradation. As advanced bioeconomy components, biorenewables derived from terrestrial, aquatic biomass and waste resources are expected to play significant roles over the next decades. This study provides an overview of potential biomass resources ranging from higher plant species to phototrophic microbial cluster, and their fundamental photosynthesis processes as well as biogeochemical carbon cycles involved in ecosystems. The review reflects empirical advances in conversion technologies and processes to manufacture value-added biorenewables from biomass and waste resources. The nexus perspective of resource-biorenewable-waste has been analysed to understand their interdependency and wider interaction with environmental resources and ecosystems. We further discussed the systems perspectives of biorenewables to develop fundamental understanding of resource flows and carbon cycles across biorenewable subsystems and highlight their spatial and temporal variability. Our in-depth review suggested the system challenges of biorenewable, which are subject to nonlinearity, variability and complexity. To unlock such system complexity and address the challenges, a whole systems approach is necessary to develop fundamental understanding, design novel biorenewable solutions. Our review reflects recent advances and prospects of computational methods for biorenewable systems modelling. This covers the development and applications of first principle models, process design, quantitative evaluation of sustainability and ecosystem services and mathematical optimisation to improve design, operation and planning of processes and develop emerging biorenewable systems. Coupling these advanced computational methods, a whole systems approach enables a multi-scale modelling framework to inherently link the processes and subsystems involved in biomass ecosystems and biorenewable manufacturing. Reviewing modelling advances, our study provides insights into the emerging opportunities in biorenewable research and highlights the frontier research directions, which have the potential to impact biorenewable sector sustainability.

Key words: biomass, biorenewable, mathematical optimisation, process design, modelling advances

Contents

1. Introduction

Driven by a range of environmental challenges e.g. climate change and resource depletion, a transition from the current fossil-based to a future sustainable bio-based economy is expected to evolve progressively in the coming decades [1]. Fossil fuels dominate the world's primary energy supply, meeting 80% of current global demands, which is projected to rise by 40% in 2035 [2]. Although unconventional oil and gas production shows that absolute fossil fuel depletion is unlikely to restrain demand, the substantially increased resource intensity of production from such new fossil fuel reserves come with a significant resource scarcity caveat [3] e.g. IEA-projected 85% increase in water demand for energy production by 2035[2]. The accelerating resource depletion is accompanied by concerns about increasing greenhouse gas (GHG) levels, where fossil fuel is a key contributor to anthropogenic GHGs [4]. At the Paris climate conference (COP21) in December 2015, 195 countries adopted the legally binding global climate agreement, which sets out the action plans to limit the global warming to well below 2°C. An innovative bio-based economy underpinned by biorenewable technologies offers significant opportunities to decarbonise economic growth, develop optimal resource use and support global adaptation efforts.

The term biorenewable refers to the bio-products derived from renewable biological resources or waste including food, bioenergy, biofuel, biochemical, biomaterial etc. A wide range of biorenewable products can be manufactured through various technology routes (Figure 2) and contribute to the bio-economy. The current bioeconomy across Europe is estimated to worth around €2 trillion [5]; whereas in the UK, the whole bioeconomy including all activities for sustainable conversion of biomass into bio-products, in total injected £220 billion added gross values and supported 5.2 million jobs in 2014 [6]. Its growth is expected to increase to £440 billion by 2030 in the UK [7]. However, as pointed out by the Stockholm Resilience Centre, human use of and impacts on the biosphere are now exceeding the multiple environmental limits [3]and planetary boundaries. The planetary boundaries is a concept proposed by Rockstrom et al [8] to define the safe operating space for humanity with respect to the Earth system and are associated with the planet's biophysical subsystems or processes. Such environmental limits have been avoided in the past by adopting technology innovation and problem shifting, e.g. industrial revolution and green revolution [9]. But current operation beyond multiple planetary boundaries does not allow for any further easy shifts [3] Thus, the burgeoning bioeconomy transformation and biorenewable sector sustainability cannot be achieved by partial system solutions but calls for whole systems approaches considering the biorenewable system complexity.

As advanced bioeconomy components, biorenewables systems can be broadly divided into five sub-system fragments - i.e. environment and natural capitals (e.g. land, water), resource production and ecosystem, biorenewable refining/manufacturing, distribution and network, waste treatment. These are often regarded and investigated as isolated sub-system fragments. In fact, they are interdependent and interlinked. Take one of the economically favourable biorenewable sectors (Figure 2) - agro-food - as an example to elaborate the resource-biorenewable-waste interdependency. Agro-foods highly depend on natural capital resources i.e. land and water. Currently, agriculture sectors account for 37% of global lands and 70% of the water consumption [10]. By 2050, the agricultural water withdrawn of 3000 km^3/yr and potential 2.8 billion ha rain-fed land use and expansion of 0.33 billion ha irrigated land are expected to take place in water-scarce regions and developing countries[10]. This brings severe land/water-competition issues with other biorenewable sectors and municipal and industrial needs in response to rapid urbanisation trends and economic growth. Moreover, rising waste generation from current agro-food sectors brings additional stress, which is equivalent to waste of 8.5% of annual water withdrawn and 28% of agricultural lands globally [11]. Thus, the agro-food production is not only dependent on and constrained by resource (land/water) availability but also interlinks with built environment (e.g.

infrastructure for waste treatment). Multiple biorenewable sectors also interact at system levels e.g. their competition on the same productive lands and water resources. Such complexity requires in-depth understanding of resource flows and processes across biorenewable sub-systems and novel system solutions to achieve resource-circularity and address their interlinkage with natural and build environments. Fundamentally, resource, biorenewable and waste form a nexus. Sitting at Natural Sciences and Engineering interface, this nexus represents a highly cross-disciplinary research frontier. Integrating empirical and computational advances, design of advanced biorenewable solutions from a whole systems perspective, offers a promising path to catalyse resource-biorenewable-waste nexus sustainability. However, no publically available study has been found to reflect the biorenewable system complexity and recent advances and prospects of computational methods for biorenewable systems research.

Here we present a critical review of biorenewable systems, bridging fundamental and applied research perspectives at Science-Engineering interface with a particular focus on biorenewable systems complexity and modelling research. This review article reflects state-of-the-art of biorenewable empirical research ranging from biological renewable resources underpinned by photosynthesis and biogeochemical cycles to biorenewable manufacturing through diverse technologies; building upon the fundamental understanding of the empirical advances, this review highlights the biorenewable system complexity and addresses the interlinkage and interdependency of sub-systems. Further, our study reviews the modelling advances to tackle such system complexity across highly interdisciplinary topics and identifies the open research challenges and gaps in the fields. This review study is concluded with future research directions on biorenewable systems modelling. The structure of the review is illustrated graphically in Figure 1.

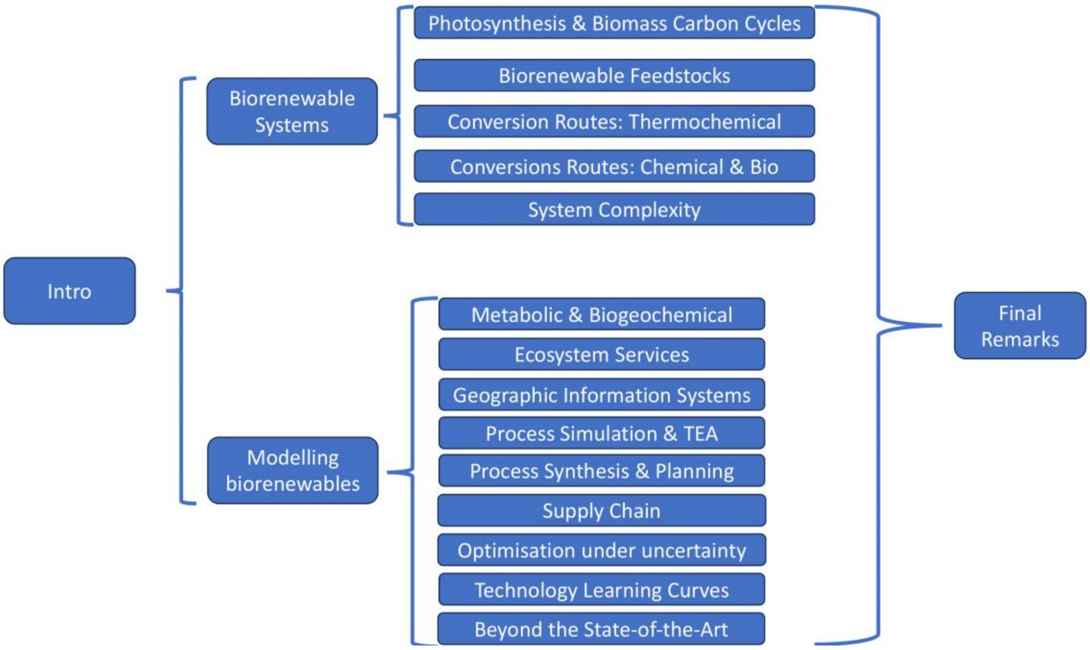


Figure 1 Diagram outlining the structure of the review.

2. Biorenewable systems

Biomass includes all complex biogenic organic and inorganic products generated by natural or technosphere and consists of 1) natural constituents originated from terrestrial or aquatic vegetation via photosynthesis or generated via animal and human food digestion; 2) technosphere products/by-products derived from processing the natural constituents above [12, 13]. In this review, biomass mainly refers to biological renewable resources (e.g. higher plant species and microbial cluster) and waste

Unlike other renewable sources, e.g. tidal energy or intermittent sources of solar and wind energy, biomass provides flexible options to overcome the supply instability and un-predictability by deriving thermal and electrical energy on demands, and offering potential for transport fuel or bio-chemical generation. Biomass is nature's successful solar conversion and energy storage system via photosynthesis to derive atmospheric CO_2-sourced carbohydrates and lignin [14]. This coupled with carbon-containing and nutrient-rich organic waste in solid (e.g. biodegradable fraction municipal solid waste (BFMSW), liquid (e.g. sewage sludge) or gas (e.g. CO_2) phases represent great potential resources.

Such a wide range of biomass organic molecules can be converted into a plethora of bio-products in the biorefineries. Biorefineries are regarded as the cornerstone of the bioeconomy (Figure 2), where various thermochemical, biochemical, and chemical routes including non-catalytic or catalytic technologies can be deployed and integrated [15]. Catalysis in particular, which has contributed to 90% of manufacturing in the petrochemical industry, will underpin future biorefinery technologies in a post-petroleum era, synthesising chemical intermediates and advanced materials from non-petroleum feedstock [14].

This section provides an overview of a range of potential biomass and waste resources, their underpinned photosynthesis, carbon cycles and various conversion pathways for biorenewables production, where the interdisciplinary research nature of biorenewable systems will be highlighted from a system perspective.

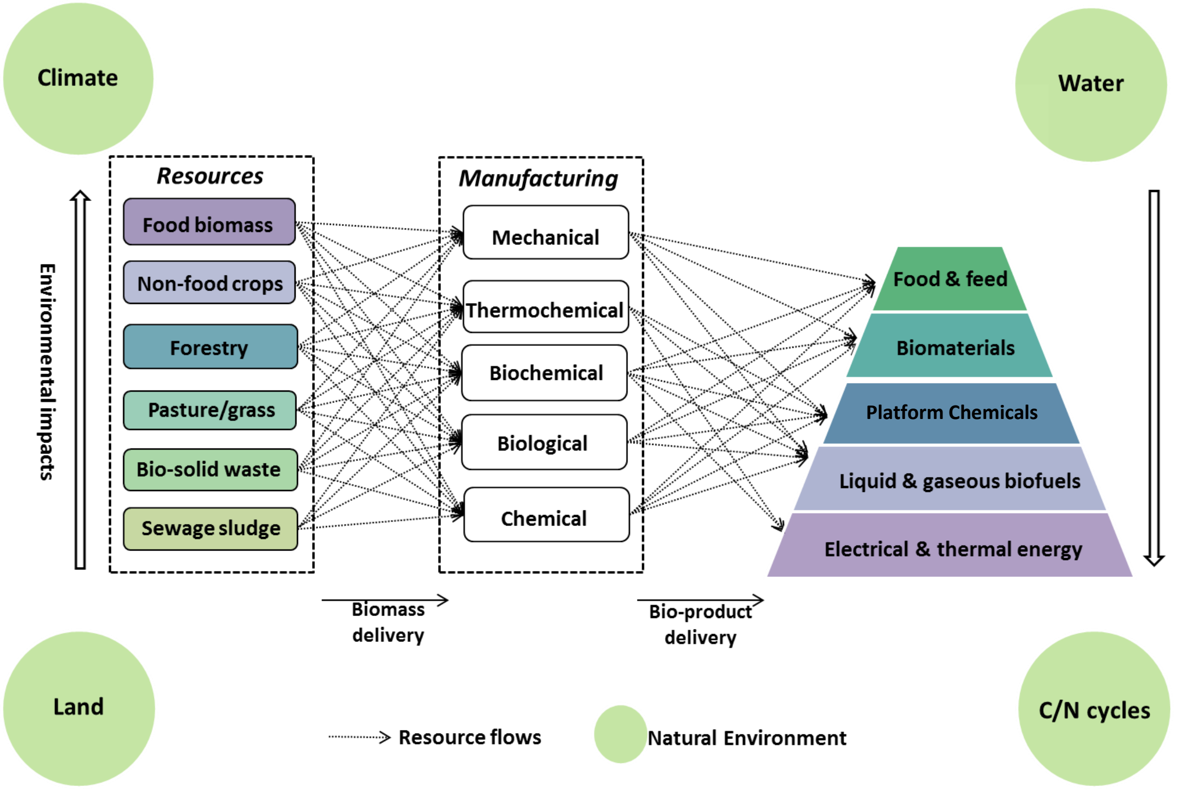


Figure 2 Biorenewable system complexity

2.1 Photosynthesis and biomass carbon cycles

Carbon as the building block of life circulates between living organisms and environments via various biochemical cycles, which refer to the carbon cycles [16]. Amongst a range of natural and anthropogenic CO_2 sinks, bio-sequestration methods particularly photosynthesis and the synthesis of bio-based products offer sustainable routes for atmospheric CO_2 assimilation. Research over past decades has advanced the understanding of photosynthesis from the initial photophysics of light absorption and excitation energy transfer to gas exchange in particular in higher plant species.

2.1.1 C3 C4 and CAM photosynthesis pathways

Photosynthesis is a redox reaction driven by light energy, in which CO_2 and H_2O are converted into metabolites and O_2, where dark and light two stage reactions are involved. Three photosynthetic pathways can be differentiated, where Calvin-Benson-Bassham (CBB) Cycle is the predominant pathway used by the vast majority of autotrophic organisms [17]. It is also referred to as C3 cycle due to three-carbon compound phosphoglycerate formed. Other two photosynthesis pathways rising from the evolutionary adaptation are Hatch-Slack cycle (also referred to as C4 cycle due to the four carbon compound oxaloacetic acid formed) [18] and crassulacean acid metabolism (CAM) photosynthesis. C3 species represent approximately 85% of higher plant species, C4 and CAM species account for 5% and 10% respectively[19]. Their photosynthetic reactions and biochemical regulation differ.

CBB cycle (Figure 3) (C3 cycle) is the largest flux of organic carbon in the biosphere and assimilates about 100 billion tons of carbon a year, which is equivalent to 15% of global atmospheric carbon [20]. CBB cycle takes place inside the chloroplast in mesophyll cell and its carbon fixation mechanism has been detailed in [20]. C3 plants such as rice, wheat, potato use CBB cycle initiated by the enzyme RuBisCO (ribulose-1,5-bisphosphate carboxylase/oxygenase), which catalyses the carboxylation of the CO_2-acceptor ribulose-1,5-bisPhosphate (RUBP) for fixing CO_2 [20]. RuBP, a 6-carbon is metabolised into two molecules of 3-phosphoglycerate (3PG) which are then metabolised into glyceraldehyde 3-phosphate (G3P), requiring ATP and NADPH synthesised from the light reactions of photosynthesis [21, 22]. G3P is a triose phosphate that serves many metabolic purposes such as synthesis of lipids, starch and amino acids [23, 24]. The final phase of the C3 cycle involves the regeneration of RuBP from a series of reactions requiring at least nine other enzymes. It is the regeneration of RuBP, requiring ATP that closes the cycle. Figure 3 presenting starch and sucrose synthesis is given as an example with detailed synthesis pathways interpreted in Supplementary Information SI-1. However, the CBB cycle is limited by the low catalysis rate of RuBisCO in carboxylation and the RuBisCO-induced competing oxygenation reaction [25], which is sensitive to environmental variables (e.g. high temperature and drought) and leads to losses of 25-30% C fixed [20]. In comparison with C4 and CAM species, C3 species particularly fast growing C3 plants demonstrated strong response to atmospheric CO_2 concentration with the enhanced yields under the elevated CO_2 concentration [26].

C4 photosynthesis represents complex nature evolutionary traits to suppress oxygenation [27] and is a series of biochemical activities partitioned between mesophyll and bundle sheath cells that are anatomically and biochemically distinct [28]. The initial carbon fixation is the carboxylation reaction catalysed by phosphoenolpyruvate carboxylase (PEPC) for oxaloacetic acids (OAA) formation from CO_2. OAA is further metabolised into malate, which diffuses into bundle sheath cell and decarboxylated to release CO_2 [27]. The CO_2 level within the bundle sheath layer can build up to over 10 times higher than the intercellular space thereby supressing the oxygenase activity of RuBisCO and the subsequent energy-wasteful oxygenation and resulting in increased photosynthetic yields [28]. Benefiting from such metabolic mechanism (elaborated in [29]), C4 plants such as maize, sorghum, and sugarcane, miscanthus and a range of C4 grass [30] demonstrate superior photosynthesis efficiency (approximately 50% higher) and nitrogen and water use efficiency (WUE) [31]. Despite only occurring in less than 5% of the global 250,000 plant species, C4 pathway contributes to 23% of terrestrial gross primary productivity [29]. Interestingly, a large percentage of grass species use C4 photosynthesis pathways. As shown in a comprehensive grass database covering 99.6% of the 11 087 grass species, 42% of those species use the C4 photosynthetic pathway with remaining 57% using C3 pathway [30].

CAM as a photosynthetic adaptation mode, features temporal separation of C3 and C4 components and nocturnal CO_2 uptake with optimised WUE, which is six-fold and three-fold higher than C3 and C4 species respectively [32, 33]. Thus CAM plants e.g. *Agave, Opuntia,* and pineapple *(Ananas comosus* (L.) Merr.) have potential to grow in arid, degraded and marginal lands for food and bioenergy purpose [34, 35]. The research on CAM metabolism can be traced back to 1960s-1970s; the biochemistry regulation as detailed in [32] may be defined as four phases [36]. In phase 1, CAM employs the PEPC enzyme for nocturnal CO_2 uptake, where the HCO_3^- resulted from carbonic anhydrase action on CO_2 is catalysed by PEPC to generate oxaloacetate. This is followed by the malate formation from oxaloacetate (catalysed by malate dehydrogenase) and its transportation into the vacuole for accumulation as malic acid. RuBisCO activation is considered to commence at the start of photoperiod, which lead to a short time window when CO_2 can be fixed by both PEPC and RuBisCO (phase 2). Malate decarboxylation for CO_2 regeneration in the intercellular spaces has been regarded as Phase 3, which is catalysed by different enzymes, depending on CAM species [37]. In phase 3, the regenerated and concentrated CO_2 is re-fixed by RuBisCO behind closed stomata. A transition to Phase 4 is accompanied by the re-opening stomata for CO_2 uptake by RuBisCO at Dusk. The duration of each phase in CAM cycle vary with species and their response to environment [38].

2.1.2 Photosystems and photosynthesis light reactions

As described in section 2.1.1 photosynthetic functions involve harvesting light to produce ATP and NADPH which are essential cofactors in downstream metabolism. Photosynthesis occurs within the thylakoid membranes inside the chloroplast. As proposed by Hill and Bendall [39], the light-dependent reactions of photosynthesis involves a photolysis reaction, powered by light energy that splits a water molecule into molecular oxygen, an electron, and an hydrogen ion. The electrons are passed through a series of carrier proteins located within thylakoid membrane and through a series of oxidation/reduction reactions, results in the production of NADPH. The passing of electrons along the electron transport chain is coupled to the translocation of hydrogen ions across the thylakoid membrane which generates a proton gradient. The proton gradient produces a proton motive force that drives the production of ATP as a result of proton movement across the thylakoid membrane through the ATP synthase enzyme [40]. ATP and NADPH are then used to fuel the dark reactions of photosynthesis, which serve the purpose of fixing CO_2 into metabolism.

The coordinated activity of two distinct photosystems, Photosystem I (PSI) and photosystem II (PSII) are involved in the light capture by oxygenic organisms. PSII or water-plastoquinone oxidoreductase, can be regarded as the first protein complex in the light reactions of photosynthesis. Its core complex is composed of chlorophyll *a* (Chl a) and β-carotene bound to several polypeptides and surrounded by an antenna complex. Electrons producing from photolysis are funnelled into PSII and passed to the next electron acceptor, cytochrome b_6f complex (*Cyt* b_6f). The *Cyt* b_6f functions to mediate the transfer of electrons towards the core reaction centre of the second photosystem, PSI via either Plastocyanin (PC) or a cytochrome c6 in *Chlamydomonas* [41]. The reaction centre core of PSI consists of a pair of Chl a molecules[42].

Two main mechanisms of electron flows between two photosystems can be differentiated i.e. linear and cyclic electron flows (LEF and CEF) (Figure 4). During LEF, electrons are transferred from water to NADP via three major transmembrane complexes: PSII, *Cyt* b_6f and PSI; whereas CEF mode only involves PSI and *Cyt* b_6f [43] and functions in generating ATP and providing a pH gradient to induce non-photochemical quenching [44]. In addition to LEF and CEF, there are several additional electron flows identified i.e. Mehler reaction [45], Plastid Terminal Oxidase (PTOX) [44].

The detailed description on PSI and PSII functions in the light reaction of photosynthesis and roles of different electron transport pathways are provided in Supplementary Information SI-1.

2.1.3 The interaction between carbon metabolism and light reactions of photosynthesis

Since the first investigation of the relationship between metabolism and photosynthesis carried out in the 1950's[46], a variety of mechanisms have since been described in the literature attempting to provide a further understanding of how carbon metabolism can regulate photosynthesis. These involve alternative electron flows [47], inter-organelle metabolite transport [23], and acclimation responses to changes in the environment [48]. The interaction mechanisms are elaborated from three aspects in the

Supplementary Information SI-1 – increasing ATP production regulated by CEF, the modulated chloroplastic NADPH by malate shunt, cytosolic and chloroplast ATP regulated by triose-phosphate.

2.1.4 Photosynthetic microbial cluster and implications on photosynthetic machineries

In addition to the C3, C4 and CAM higher plant species, the phototrophic microbial cluster also play significant roles in biological CO_2 sequestration. Microbial phototrophs include microalgae, oxygenic and anoxygenic phototrophic prokaryotes, with the later encompassing taxonomically diverse groups of Bacteria and Archaea [16, 49, 50]. The diversity and some characteristics of the photosynthetic microbial cluster are shown in Table 1. Microalgae and cyanobacteria are the only microorganisms able to perform a plant-like oxygenic photosynthesis, assimilating CO_2, producing organic carbon, and using two photosystems (PSI and PSII) which function in series connected via an electron transfer chain. Anoxygenic phototrophs perform photosynthesis without production of molecular oxygen and they do not use water as electron donor. Instead, they use a wide variety of inorganic and reduced organic carbon compounds as photosynthetic electron donors. In addition, anoxygenic phototrophs show variable protein and pigment compositions in their photosynthetic apparatuses. Although anoxygenic phototrophs thrive in all environments, their contribution to global primary production is small compared to the significance of oxygenic photolithotrophy. It has been concluded that aerobic anoxygenic photoheterotrophs do not contribute significantly to photosynthetically driven energy fluxes in eutrophic and mesotrophic temperate and subtropical aquatic environments [51], even though their contribution to the marine carbon cycle may be significantly higher in the oligotrophic open sea [52]. However, this type of phototrophy seems to be more significant on the phyllosphere of terrestrial plants [53]. In aquatic environments, almost all net primary productivity is contributed by oxygenic photolitotrophs, with only 0.5 – 1 % attributable to anoxygenic photolithotrophs and chemolithotrophs [54]. Furthermore, the contribution of cyanobacteria to oceanic primary productivity may be greater than it was thought previously. Taxa such as *Acaryochloris marina*, a Chl *d*-producing prokaryote which is widely distributed in coastal areas, and Chl *f*-producing cyanobacteria (*e.g. Halomicronema hongdechloris*) can use far-red light for growth [55], and the contribution of far-red light photosynthesis to the primary productivity in marine environments has not been estimated [56]. In photosynthetic organisms there are three major chemical groups of light-harvesting pigments, chlorophylls, carotenoids and phycobilins, which perform light absorption at different spectral regions. In addition, carotenoids protect chlorophyll against photo-oxidative damage in both plant and bacterial photosynthesis [57]. Mirkovic et al [58] gave a comprehensive overview on the performances of the different light-harvesting machineries present in photosynthetic organisms thriving in diverse environments.

Although the research in microbial photosynthesis and the comparison with higher plant-like photosynthesis can be traced back to 1930s [59], there have been very few literature discussing the significance of the photosynthetic microbial cluster in the biological sequestration of CO_2. However, the potential of microbial cluster in photosynthesis, CO_2 sequestration and bioeconomy has started gaining research attention in the past few years. A comprehensive review has been conducted by Mohan et al. [16] on microbial CO_2 capture, which has led to a proposed biorefinery model catalysed by microorganisms. To date, six CO_2 fixation pathways have been identified, which function under aerobic conditions (the CBB cycle, the 3-hydroxyproprionate pathway and the 3-hydroxypropionate-4-hydroxybutyrate cycle) and under anaerobic or microaerophilic conditions (the reductive tricarboxylic acid cycle, the reductive acetyl-CoA pathway, and the dicarboxylate-4-hydroxybutyrate cycle) [60]. In plant, algae and oxygenic photosynthetic bacteria the Calvin–Benson–Bassham (CBB) cycle is the predominant CO_2 fixation pathway, but this pathway is also used by a variety of anoxygenic phototrophs and non-photosynthetic microorganisms [16]. Within the Domain Bacteria, the CBB pathway has been demonstrated to operate in representatives of green-sulfur bacteria, cyanobacteria, alpha-, beta- and gamma-proteobacteria and Actinobacteria [60]. In Actinobacteria capable of autotrophic growth (*e.g.* some strains of *Pseudonocardia*) the CBB cycle is the only CO_2 fixation pathway that has been reported [61].

Cyanobacteria and eukaryotic phytoplankton are the most important inorganic carbon fixers in the oligotrophic ocean and together contribute up to 50% of the net primary productivity in the ocean, playing a key role in biogeochemical cycling [62]. Here the biogeochemical cycling defined as the pathways, by which chemical substances and elements move through the biotic and abiotic compartments of Earth. These microphototrophs have evolved sophisticated and highly efficient systems called CO_2-concentrating mechanisms (CCMs) to actively capture inorganic carbon (C_i) from the nearby environment and increase the CO_2 concentration near RuBisCO by up to 1000-fold [63], thus counteracting the low solubility and diffusivity of dissolved C_i and the intrinsic limitations of RuBisCO (slow enzyme kinetics, poor discrimination between CO_2 and O_2 as substrates, and loss of photosynthetic efficiency due to photorespiration) [64, 65]. Microalgal and cyanobacterial CCMs include C_i transporters and subcellular microcompartments that contain RuBisCO and carbonic anhydrases (carboxysomes in Cyanobacteria, pyrenoids in algae). In Cyanobacteria, the CCM is composed by three active bicarbonate transporters: the medium-affinity Na^+-dependent HCO_3^- transporter (BicA), a high affinity HCO_3^- transporter (BCT1 complex) and a high affinity, Na^+-dependent HCO_3^- transporter (SbtA). Furthermore, there are two thylakoid-bound, active transporters of CO_2 (NDH-I_3 and NDH-I_4) and at least three ion exchangers [65, 66]. The C_i pumps concentrate HCO_3^- in the cytoplasm and the carbonic anhydrase dehydrates the cytosolic bicarbonate pool to CO_2. The CO_2 generated within the carboxysome is fixed into organic carbon by RuBisCO in the CBB cycle.

Recent advances in biotechnology and synthetic biology have assembled a toolbox for genetic engineering of cyanobacteria, eukaryotic algae and offer tailored chloroplast transformation tools for the redesign of some photosynthesis aspects in crop species. Via manipulating carbon-fixation pathways and redesigning the C3/C4 photosynthesis, gains in terrestrial crop productivity can be achieved [67]. The integration of a complete and functional cyanobacterial and microalgal biophysical CCMs and the engineering of particular CCM components into C3 plants to improve the efficiency of photosynthetic CO_2 uptake have been discussed [68], although much research is still needed on the characterization of CCM genes, components and regulatory processes, as well as testing transgenic lines under realistic growth conditions [65, 69]. As oxygenic phototrophs, cyanobacteria offer an attractive experimental platform for improving CO_2 fixation in higher plants, because of their fast growth rates, their facile genetics, their evolutionary relationship to plant plastids and availability of genome sequences [70]. Besides, the CCMs of cyanobacterial model organisms have been extensively studied [71, 72]. Recent progress in engineering CO_2-fixation pathway in C3 plants includes, for example, the introduction of cyanobacterial bicarbonate transporters into plant chloroplasts, reconstruction of cyanobacterial carboxysomes and associated transporters in *Escherichia coli* and the generation of transgenic tobacco plants containing cyanobacterial RuBisCO [73-75]. However, the introduction of eukaryotic microalgal biophysical CCMs to vascular plants may have a better potential because they share many photosynthetic and molecular characteristics, and their closer evolutionary relationship [63].

Table 1 Characteristics of major groups of phototrophic prokaryotes.

Type/Taxon	**Electron donors**	**Photopigments**	**Carbon source**	**Photosynthetic reaction center (RC)[1]**	**Physiological type**	**References**
PROKARYOTES						
Anoxygenic						
Purple sulfur bacteria (γ-proteobacteria)						
Chromatiaceae *Ectothiorhodospiraceae*	S^{2-}, S^0, $S_2O_3^-$, H_2, Fe^{2+}, NO_2^-	BChl *a* or *b*	CO_2, organic	Type II RC	Phototrophic, some chemoorganotrophs and chemolithotrophs	[50, 76]
Purple nonsulfur bacteria						
α- and β-proteobacteria	H_2, organic compounds, low levels of S^{2-}, a few	BChl *a* or *b*	CO_2, organic	Type II RC	Phototrophic, some chemoorganotrophs and chemolithotrophs	[50, 76]

	species $S_2O_3^-$, Fe^{2+}					
Green sulfur bacteria						
Chlorobiaceae	S^{2-}, $S_2O_3^-$, H_2, a few species Fe^{2+}	BChl *c*, *d*, or *e*	CO_2, organic	Type I RC	Photolithotrophs	50, 77, 78
Phylum Chloroflexi, class *Chloroflexi*						
Chloroflexaceae	S^{2-}, H_2, organic	BChl *a*, *c*	CO_2, organic	Type II RC	Photoheterotroph, some strains photoautotrophs, chemoheterotroph	78, 79
Oscillochloridaceae	S^{2-}, H_2	BChl *a*, *c*, or *d*	CO_2, organic	Type II RC	Photolithoautotroph, photolithoheterotroph	79, 80
Roseiflexaceae	Organic, Low levels of S^{2-}	BChl *a*	Organic	Type II RC	Photoheterotroph, some species chemoheterotrophs	79, 81-83
Heliobacteriaceae	Organic	BChl *g*	Organic	Type I RC	Photoheterotroph; neutrophilic species are capable of chemotrophic growth	50, 78, 83
Archaea						
Halobacteriaceae						
Halobacterium salinarum and probably a few other species	None – generates proton gradient	Bacteriorhodopsin (retinal ~570 nm)	Organic	Bacteriorhodopsin	Photoheterotroph[2]	84, 85
Oxygenic						
Cyanobacteria[3]	H_2O, S^{2-}	Chl *a*, phycobilins	CO_2	Type I + II RC	Photolithoautotroph	50, 86
Prochlorococcus, *Prochlorothrix* and *Prochloron*	H_2O	Chl *a*, *b* [4]	CO_2	Type I + II RC	Photolithoautotroph	50, 87, 88
Acaryochloris marina	H_2O	Chl *a*, *d* [5], α-carotene, phycobilins	CO_2	Type I + II RC	Photolithoautotroph	56, 89
EUKARYOTES						
Microalgae						
Bacillariophyceae	H_2O	Chl *a* and *c*, fucoxanthin	CO_2, organic carbon (mixotrophs)	Type I + II RC	Photoautotrophs; various diatoms have been reported to grow mixotrophically	90-94
Chlorophyceae	H_2O	Chl *a* and *b*,	CO_2, organic carbon (mixotrophs)	Type I + II RC	Photoautotrophs; several taxa are mixotrophs	94-98

		β- and γ-carotene, xanthophylls				
Chrysophyceae	H_2O	Chl *a*, Chl c_1 and c_2, β-carotene, xanthophylls	CO_2, organic matter (mixotrophs)	Type I + II RC	Photoautotrophs, mixotrophophs (osmotrophy, phagotrophy)	[95, 99]

[1] *Photochemical reaction centre: a multisubunit photopigment-protein complex in which electromagnetic energy from sun is transduced into redox chemistry.*

[2] *Halobacteriaceae generally lead an aerobic chemoheterotrophic life, but under conditions of low oxygen Hbt. salinarum can produce energy using bacteriorhodopsin-driven photosynthesis.*

[3] *Some Cyanobacteria conduct anoxygenic photosynthesis with sulfide as an electron donor.*

[4] *Prochlorococcus possesses divinyl-Chl a and divinyl-Chl b*

[5] *BChl, bacteriochlorophyll; Chl, chlorophyll. The chemical structure and absorption spectra of photosynthetic pigments are available in [58]. Chl d is its major pigment.*

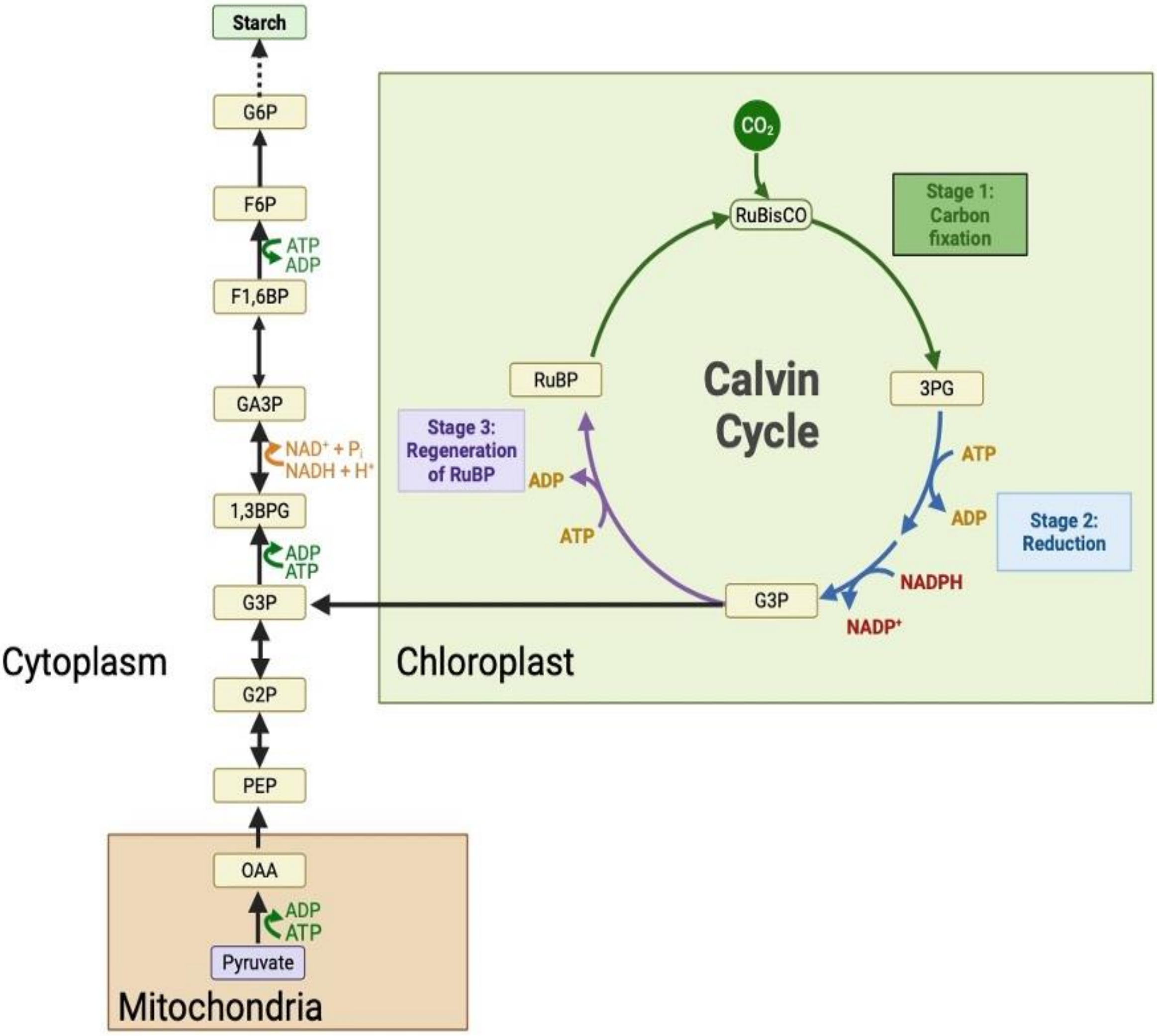
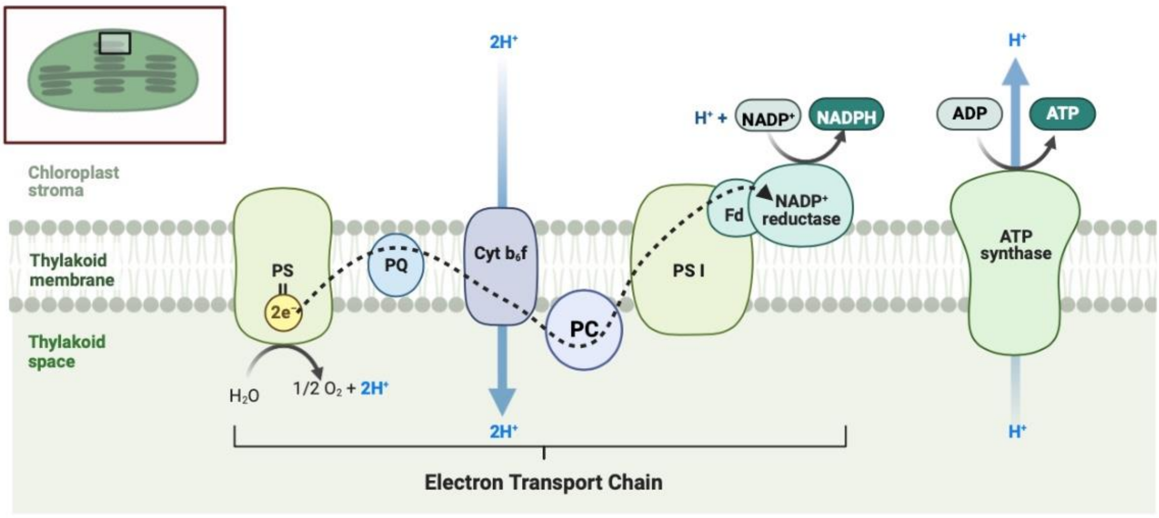


Figure 3 The light independent reactions of photosynthesis; carbon fixation to starch synthesis

stage of the Calvin-Benson-Bassham cycle (referred here as the Calvin cycle) involves the fixation of RuBisCO and assimilation into the triose phosphate, 3PG, within the chloroplast. The second stage of the Calvin cycle is reduction of 3PG into G3P. G3P can stay within the Calvin cycle, or leave the chloroplast and join the gluconeogenesis pathway for metabolism into starch synthesis. The dashed line represents multiple metabolic steps. The third stage of the Calvin cycle involves the regeneration of RuBP which then closes the cycle[2324] *.Rectangles represent metabolites and the only enzyme highlighted for simplicity, is RuBisCO, located within the Calvin cycle. Abbreviations: 1,3BPG: 1, 3-biPhospho-D-glyceroyl phosphate, 3PG 3, Phosphogluterate: F6P: fructose 6-phosphate,, F1,6bp: Fructose1,6 bisphosphatase, G1P: Glucose 1-phosphate, G2P: 2-phosphoglycerate,, G3P: Glyceraldehyde 3-phosphate, G6P: Glucose 6 phosphate, GA3P: Glyceraldehyde 3-phopshate, OAA; Oxaloacetate, PEP; Phosphopenolpyruvic acid, RuBisCO: RuBisCO,, RuBP: Ribulose 1, 5-bisphosphate.*

A



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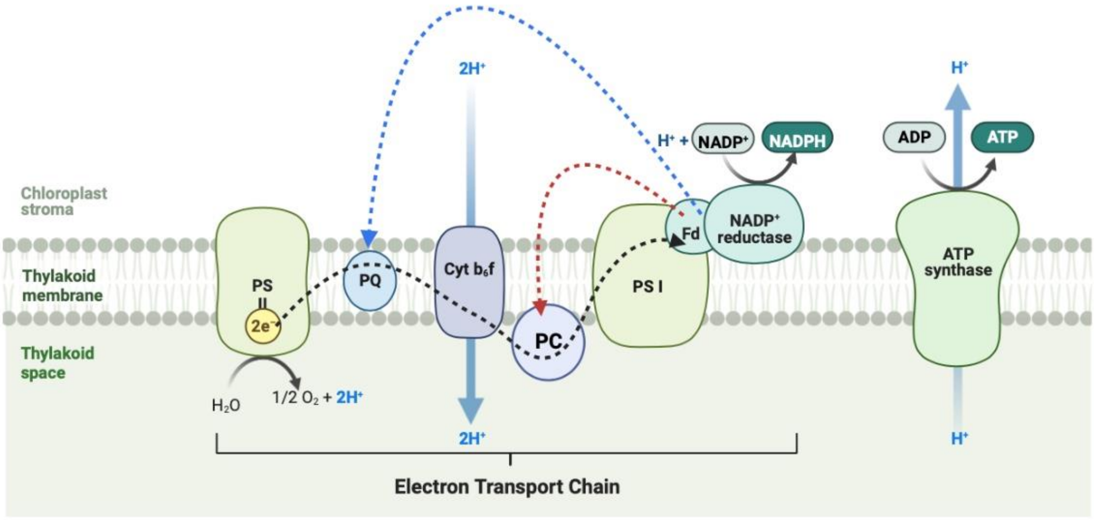


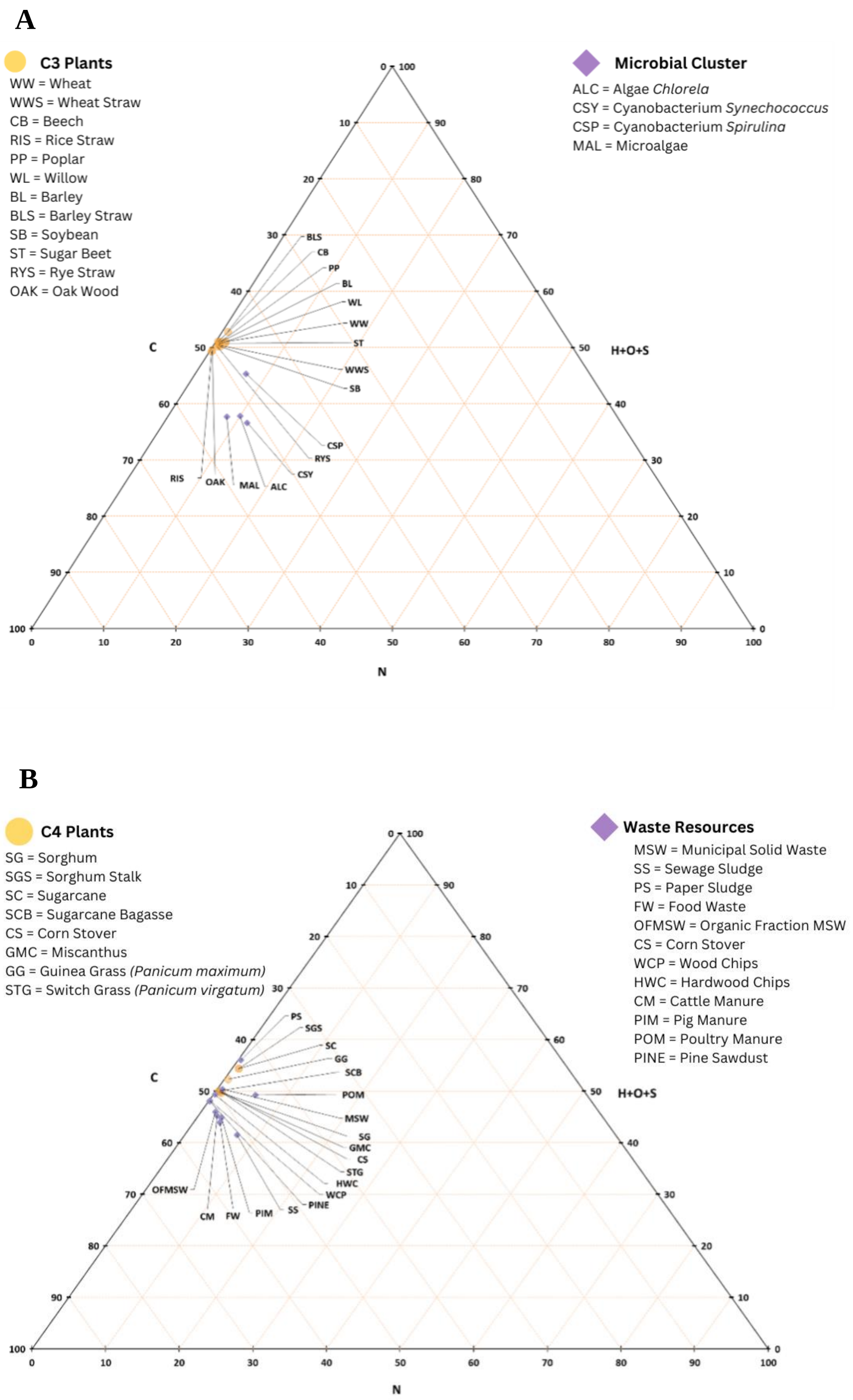
Figure 4 A schematic model of the light reactions of photosynthesis A) during linear electron flow B) sustaining a cyclic electron flow

In linear electron flow, electrons from the photolysis of H_2O *are passed along an electron transport chain resulting in the production of ATP and NADPH from the oxidation of water. In a cyclic electron flow electrons are injected back into the electron transport chain and mediated by ferredoxin via the PGR5 pathway (blue dashed line) or NDH pathway (red dashed line). As such, NADP-reductase is no longer the recipient of electrons,* *resulting in the regulation of NADPH synthesis Abbreviations: Cyt b_6f: Cytochrome b_6f complex, Fd: Feredoxin, PC: Plastocyanin PSI: Photosystem I, PSII, Photosystem II, PQ: Plastoquinone.*

2.2 Biorenewable feedstock: terrestrial vs. aquatic biomass, wastes

Biomass can be categorised based on their origins as terrestrial and aquatic biomass, as well as waste resources. Although the bio-product beneficial effects have been recognised [100], there is no consensus on the estimated future biomass supply-demand balance. As discussed in section 2.1, the terrestrial or aquatic phototrophs invest a fraction of photosynthetic CO_2 uptake by the ecosystem (termed as gross primary productivity (GPP)) on the biomass production. But their carbon use efficiency (CUE) and fixation as biomass resource vary with environmental, spatial and temporal factors (e.g. nutrient availability, climate zone) [101], with CUE ranging between 0.3 and 0.61 (Table 2). If using net primary production (NPP, quantified as the net amount of carbon assimilated in a given period by vegetation) [102] as an indicator of the ecosystem carbon fixation and biomass supply, the current terrestrial NPP adds approximately 1.2×10^{11} ton dry vegetative biomass annually (50% C assumed), storing 2200 EJ energy in plant material [103, 104], where non-agricultural terrestrial NPP contributes to nearly 75% (4.5×10^{10} ton carbon fixation) [105].

Based on their key chemical composition, biomass can be largely grouped as sugar and starch, lignocellulose, other carbohydrate, oil, lipid and protein [106]. Driven by a range of factors, including biomass species and parts, photosynthetic pathways, climate and soil variables and agricultural management (e.g. agrochemical inputs and field operations), the chemical composition vary significantly between different biomass groups [13]. As demonstrated in Figure 5, on the dry-weight ash-free basis (DAF), the carbon contents in higher plant species (C3 and C4 plants) fall into the range of 44.7-50.5% whereas the microbial cluster showed higher C contents (above 50%). The waste sectors represent another C-rich resource where the C contents vary from 43.6% to 52.5% (DAF basis).In general, microbial cluster is the most N nutrient rich source (around 10%), followed by organic-N or ammonium-N containing waste resources (food waste, sludge, and manure with 4-7% N contents). Higher plant species show very low N contents, ranging from 0.4% to1.5% (DAF basis). Therefore, the resource C:N ratios ranked from low to high are microbial cluster < waste < higher plant species (C3/C4 plants). Such elemental analyses along with other physiochemical properties and chemical composition can provide biomass performance indicators and design basis for biorenewable systems as they influence the conversion technology performance at process levels and the associated supply chain and network design at system-levels. Particularly for biological routes (e.g. anaerobic digestion), carbon and nitrogen are important substrates and nutrients for the microbial syntheses, which play important roles in the bio-conversion processes.


A
C3 Plants
WW = Wheat
WWS = Wheat Straw
CB = Beech
RIS = Rice Straw
PP = Poplar
WL = Willow
BL = Barley
BLS = Barley Straw
SB = Soybean
ST = Sugar Beet
RYS = Rye Straw
OAK = Oak Wood
Microbial Cluster
ALC = Algae *Chlorela*
CSY = Cyanobacterium *Synechococcus*
CSP = Cyanobacterium *Spirulina*
MAL = Microalgae
C
H+O+S
N
BLS
CB
PP
BL
WL
WW
ST
WWS
SB
CSP
RYS
CSY
RIS
OAK
MAL
ALC
0
10
20
30
40
50
60
70
80
90
100
B
C4 Plants
SG = Sorghum
SGS = Sorghum Stalk
SC = Sugarcane
SCB = Sugarcane Bagasse
CS = Corn Stover
GMC = Miscanthus
GG = Guinea Grass *(Panicum maximum)*
STG = Switch Grass *(Panicum virgatum)*
Waste Resources
MSW = Municipal Solid Waste
SS = Sewage Sludge
PS = Paper Sludge
FW = Food Waste
OFMSW = Organic Fraction MSW
CS = Corn Stover
WCP = Wood Chips
HWC = Hardwood Chips
CM = Cattle Manure
PIM = Pig Manure
POM = Poultry Manure
PINE = Pine Sawdust
C
H+O+S
N
PS
SGS
SC
GG
SCB
POM
MSW
SG
GMC
CS
STG
HWC
WCP
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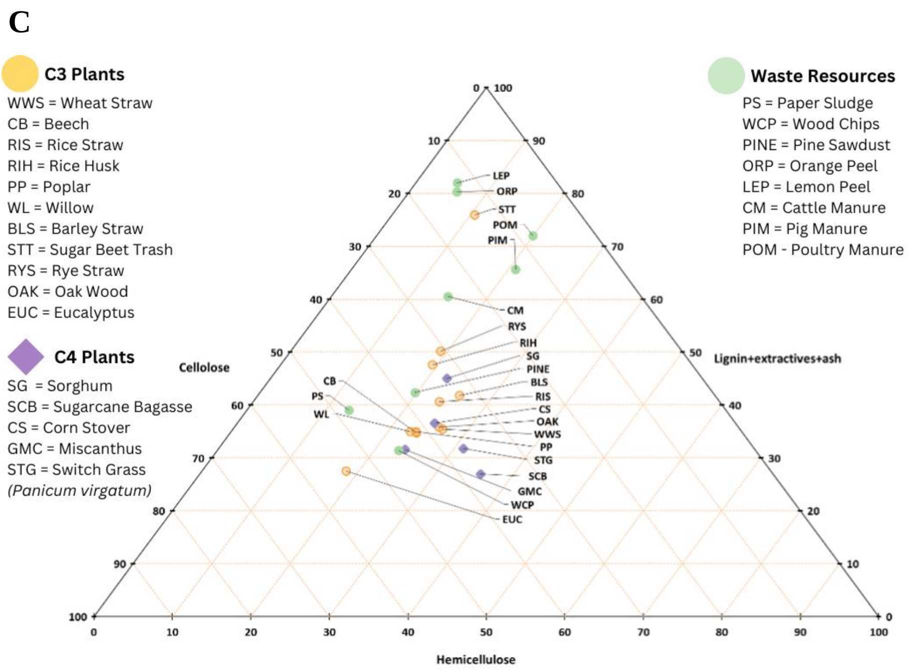


Figure 5 Elemental analyses (A,B) and chemical composition (C) on dry-weight and ash-free basis
Data are derived from Phyllis2 database [107] *and reference*[108], *and the composition data of wood chips* [109], *pine sawdust* [110], *orange and lemon peels* [111], *paper sludge* [112], *switch grass* [113] *manure* [114], *food waste*[115].

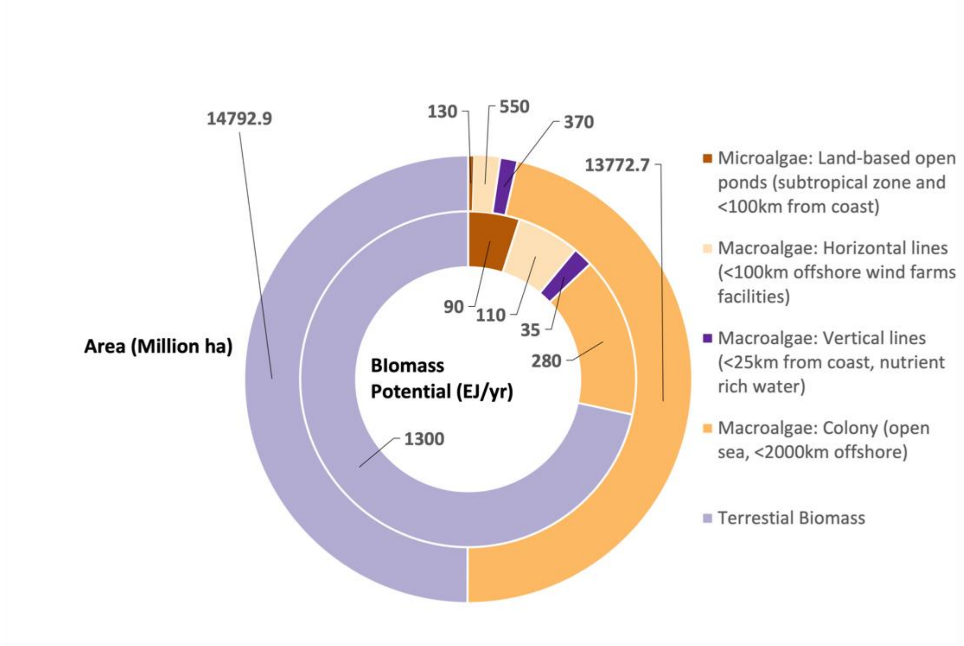


Figure 6 Biomass potential [116, 117]

2.2.1 Terrestrial biomass

Terrestrial biomass refers to a range of food and non-food resources grown on terrestrial lands including arable, grass, forestry lands or abandoned lands. Amongst biomass resources, this is the most widely investigated biomass category. Despite of the focus on bioenergy, previous studies indicated the uncertainties in the global terrestrial biomass estimates, varying from around 30 EJ to over 1500 EJ per year [118, 119]. Searle and Malins [119] reviewed the key bioenergy modelling articles and based on the land constraints, theoretical resource potential, spatially-explicit biomass production costs and governance, revised the annual biomass estimates for energy as 60-120 EJ by 2050 and suggested that bio-based ambition is difficult to achieve sustainably. Alternative to business as usual scenarios, previous research explored the effects of agricultural intensification and optimised management on future terrestrial supply-demands [120, 121]. Mauser et al. [122] projected that the agricultural intensification and optimised land allocation will lead to nearly 40% increase in the global biomass production potential, being sufficient to satisfy 2050 demands without cropland expansion. Tilman et al. [123] and Muller et al. [120] highlighted the importance of sustainable intensification and optimal nutrient and water management in meeting the agricultural food demands with minimal environmental impacts. Galan et al. [124] found terrestrial biomass cultivation compared favourably with direct air capture as a cost-effective method of extracting carbon dioxide from the atmosphere. Campbell et al [125] noted the potential of abandoned land for cultivating bioenergy crops. In addition to management strategies above, redesign of photosynthesis along with breeding approaches has been also proposed as terrestrial biomass solutions to bridge supply-demand gaps [67], considering the limited natural genetic variation in the enzymes and processes of plant photosynthesis.

The bio-products derived from terrestrial food crops are regarded as first-generation (so called 1G) biorenewables whereas those from terrestrial non-food lignocellulosic biomass can be classified as second-generation (2G) biorenewables. Generally, a range of undesirable traits of terrestrial plants particularly 1G crops constrain the sustainability of the terrestrial-dependent biorenewable sectors. Terrestrial crops suffer from inefficient CBB cycles of CO_2-fixation, small fractions of edible biomass, and a high vulnerability to biotic and abiotic stress (e.g. pests and pathogens, flood and drought). Terrestrial biomass not only are stressed by increasing demands but also face the land-water resource scarcity and environmental and social constraints due to their intensive land and water inputs. Take 1G bio-products as an example. Currently, agriculture sectors account for 37% of global lands and 70% of the water withdrawn for human use [10]. As estimated by Mekonnen et al. [126], the global average water footprint for food crops range between 224-4363m^3/ton where cereal crops were shown as main water consumers. By 2050, the agricultural water withdrawn of 3000 km^3/yr and potential 2.8 billion ha rain-fed land use and expansion of 0.33 billion ha irrigated land are expected to take place in water-scarce regions and developing countries[10]. This brings severe resource-competition issues with municipal and industrial needs in response to rapid urbanisation trends and economic growth.

Terrestrial biomass are dominated by sugar crops (e.g. sugarcane, sugar beet), lignocellulosic feedstock (e.g. wheat straw, willow, miscanthus) and oil crops (e.g. rapeseed, soybean, sunflower, Jatropha) to derive monosaccharide (e.g. glucose, sucrose), polysaccharide (e.g. starch, cellulose and hemicellulose), lignin, protein, lipid, fatty acids and minerals. Amongst terrestrial biomass, lignocellulosic is the predominant biorenewable resource [108, 127] including agricultural residuals, forestry, lignocellulosic energy crops, grass etc., where cellulose is estimated as the most abundant organic compound on earth [128]. The main structural compound groups comprising the lignocellulosic plant cell wall are cellulose, hemicellulose and lignin. In addition, there are other non-structural components within the plant cell wall, such as extractives, protein, ash, and pectin, varying greatly with species, tissue, plant maturity, harvest times, and storage. Figure 5C reveals diverse lignocellulosic biomass composition, where the cellulose and hemicellulose contents range between 18-73% (dry basis). C3 and C4 higher species sit at the upper range of the cellulose and hemicellulose composition (37.1-54.1% and 22.8-31.2% respectively), which demonstrate their great potentials for polysaccharide bioconversion. However, the technology design to convert lignocellulosic biomass to value-added biochemical remain a big challenge due to natural recalcitrance, chemical composition and structure complexity as well as the different re-activities of the 2G compound groups [127]. As demonstrated in Table 3, three compound groups differ significantly. Cellulose is formed by the D-glucose subunits which are arranged in a crystalline structure of microfibrils, thus relatively resistant to thermal decomposition; whereas hemicellulose consist of different sugar monomers organised in random amorphous structure, thereby is the least thermally stable component. Due to the complex and interconnected linkages between p-hydroxyphenyl, syringyl and guaiacyl units in the three-dimensional polyphenolic polymer [129, 130], lignin shows high thermal stability with decomposition occurring across a wide temperature range [131]. The bio-decomposition process highly depends on the compound complexity. Different from cellulose, which decompose catalysed by enzyme cellulase, hemicellulose complexity requires a set of enzymes to achieve decomposition [132]. Lignin is rather inert to degradation due to its aromatic nature and highly cross-linked polymer network [133]. In the nature carbon cycle, white-rot fungi and ligninolytic bacteria deploy different types of enzymes degrading lignin (see Table 3). The state-of-the-art progress in ligniolytic bacteria and fungi enzyme systems, their delignification activities as well as potential applications in biotechnology have been well studied and summarised by the comprehensive reviews conducted by Pollegionin et., [134] and de Gonzalo et al. [130]. The reactivity of three compound groups in the presence of chemical reagents and non-thermal triggers have been widely investigated. Advances in reactivity and mechanisms underlying lignin depolymerisation and catalytic valorisation as well as the relationship between lignin structure and catalyst performance have been well presented in recent comprehensive reviews by Ma et al [135] and Rinaldi et al. [136]. For the polysaccharide components, in addition to the decomposition catalysed by different chemical reagents via biochemical and thermochemical routes [127], emerging research on the depolymerisation activated by non-thermal sources (e.g. mechanical force, electric or magnetic field, waves, light, in situ heat) have been also highlighted [137]. The differed reactivity of three structural components are important parameters for designing biorefinery based on the processability of the 2G biomass.

Above lignocellulose biomass is given as an example to analyse the biomass composition complexity. Overall, terrestrial biomass offer promising resources underpinning bioeconomy development and can be processed via diverse technologies and converted to value-added products. However, as summarised in Table 2, the sustainable exploition and development of terrestrial biomass still remain a challenge, where the resource-efficiency and other environmental sustainability are important design criteria for process and supply chain planning. This will be discussed in following sections.

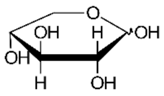
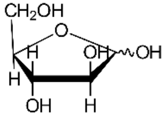
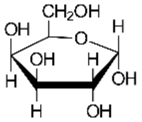
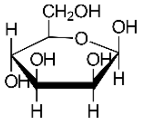
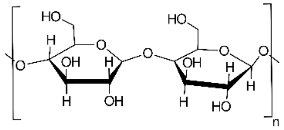
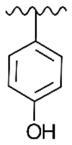
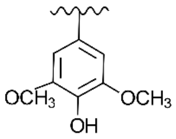
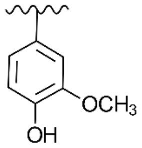
Table 2 Biomass resource comparison

	TERRESTRIAL	AQUATIC	WASTE	REFERENCES
RESOURCES	-C3, C4 and CAM higher plant species (food crop, non-food crops, forestry, grassland)	-Microalgae -Macroalgae and seagrass - Cyanobacteria	-Waste gases (e.g. C-containing gas) -Solid phase (e.g. BFMSW - forestry/agriculture waste) -Liquid phase (e.g. wastewater)	[138]
COMPOSITION	-Monosaccharide (e.g. glucose, sucrose) -Polysaccharide (e.g. starch, cellulose and hemicellulose) -Lignin, -Protein, lipid, fatty acids and minerals	-Lipids -Proteins -Carbohydrates	- Monosaccharide -Polysaccharide -Lignin, protein, lipid, fatty acids -Minerals, and inert, contamination (e.g. heavy metals)	
POTENTIAL AND REGIONS	-Potential of 60-1500 EJ/yr by 2050 -Regions: Central and Southern Africa; South America, India, Europe, USA and Canada, Russia, Australia particularly marginal lands	- Potential estimated as 515 EJ/yr by 2050 - Regions: Open sea (Caribbean Sea, South Atlantic Ocean, Indian Ocean, Mid Pacific and South Pacific Ocean) and costlines (EU, SEA, Latin Merica, North America, Africa west coastline)	- Agriculture and forestry residue potential of140-170 EJ/yr by 2100 - OFMSW estimated as 17.8EJ/yr [2] - Wastewater 3322.7km3 by 2050 -Regions: low-middle income countries; urban areas.	[116, 117, 125, 139-141]
PHOTOSYNTHESIS AND CUE[1]	-Photosynthesis: CBB/C4/CAM cycles; -CUE = 0.43-0.61	-Photosynthesis: CBB cycle -CUE =0.26-0.3 (aquatic microbial cluster)	Not applicable	[101, 142-146]
CULTIVATION	-Growth on soil; -Farm machinery for field operation	-Growth on aqueous nutrient media; -Growth in engineered systems (open ponds or photo-bioreactors)	Not applicable	[147]
LAND UTILISATION	-Potential land competition with other sectors e.g. food	-No land competition with food	-No land competition with food	[147-149]
WATER UTILISATION	-Irrigation water -Rainwater	-Freshwater -Salt water or harsh condition - Non-portable water	Not applicable	[147]
RESOURCE INPUTS	- Atmospheric CO_2 -Artificial or organic fertilisers	-Wide range of CO_2 (e.g. flue gas from power plant, ethanol plants, H_2 plants, biorefineries, cement plants, fertiliser/ammonia plants);	Not applicable	[147, 148]
CIRCULAR-SYSTEM POTENTIAL	No, nutrient loss through C/N cycles, leads to atmospheric and waterborne emissions	Yes, strains grown on wastewater (WW); potential 90% nutrient recovery	Yes, carbon and nutrient recovery from waste	[150-152]

REMEDIATION	Phytoremediation potential (e.g. heavy metals, N and P pollution).	Bioremediation potential (e.g. heavy metals, organic pollution).	Not applicable	151-156
HARVESTING CYCLES	Annual or perennial plants with less frequent harvesting cycles	Frequent harvesting (e.g. weekly, monthly)	Not applicable	147
STORAGE	Long-term (years)	Short-term (days)	Short term (days)	147
TRANSPORTATION	Relatively dry	Low solid concentration	Vary with waste	
CONVERSION ROUTES	Biochemical routes; thermochemical routes; chemical and mechanical routes			
MODELLING RESEARCH CHALLENGE	Overarching models from metabolism to biophysical and biogeochemical processes	Multi-scale overarching models and spatial variability	Waste sector complexity and data availability	

1. *CUE is defined as ratio of growth to carbon assimilation for microbial cluster* [142] *and ratio of NPP to GPP for higher plant* [157]. *Considering the themodynamic constraint, CUE upper limit for microbial system is 0.6.*
2. *Calorific value of organic fraction MSW is derived from* [158]

Table 3 Lignocellulosic biomass reactivity

		Hemicellulose				**Cellulose**	**Lignin**		
Chemical structure									
		Xylose	Arabinose	Galactose	Mannose	Cellulose	p-hydroxyphenyl	syringyl	guaiacyl
Elemental analyses (wt.%) [159]	C	44.3				44.5	56.6		
	H	5.3				5.6	4.2		
	O	44.9				49.5	37.1		
	N	0.3				0.3	0.5		
	S	0				0.1	1.6		
	Volatile	75.3				94.1	49.9		

Proximate analysis (wt %) [159]	Fixed carbon	19.9	5.9	40.1
	Ash	4.8	0	10
Thermal decomposition [1]		lignin > cellulose > hemicellulose		
		220-315°C	315-400°C	160-900°C
Bio-degradation /decomposition		Hemicellulase e.g. endoxylanases, endomannanases, xylosidases, glucosidases, arabinosidases, galactosidases, mannosidases and glucuronidases [2]	Cellulase	Heme peroxidases and laccases from ligniolytic fungi and bacteria as well as other bacteria enzymes [3]
Reactivity in solvents [4]		-Inorganic acid or organic acids; dilute acids (e.g. 0.175% (wt/vol) H_2SO_4) more effective on hemicellulose; at low temperature and short reaction time, concentrated acid is more preferable for cellulose. -Ionic liquid -Organic solvents e.g. reagents bearing –OH or –SH groups -Alkaline -Supercritical water (existence of water under elevated temperature and pressure, where the ordered hydrogen bonds tend to become weaker and break to form clusters of concentrated molecules)		-Acid e.g. peroxy acids -Organic solvents e.g. 35-70% (wt/vol) ethanol - kraft solvent (Na_2S/NaOH) - Hydrogen peroxide - Chlorine and Chlorine dioxide - Alkaline -Ionic liquid particularly with strong hydrogen-bonding basic anions -Hydrothermal liquefaction oil
Reactivity in solid [5]		-solid acids(e.g. amberlyst)		- Solid acid
Reactivity in gaseous phase [5]		-Gaseous acid (e.g. HCl) -Ionised gas by non-thermal atmospheric plasma -Chemical vapour		-Ozone -Oxygen -Chlorine -H_2 (catalytic hydrogenolytic depolymerisation)
Reactivity in physical energy [6]		- Mechano-chemical - Microwave enhanced - Ultrasound and sonication - CO_2-laser radiation		-Ultrasound -Macro-wave enhanced (e.g. ionic liquid)

1. *References* [131, 160-162]*;*
2. *Reference* [132]*;*
3. *References* [129, 130, 134] *- heme peroxidases from white rot fungi include manganese peroxidases, versatile peroxidases, and dye-decolorizing peroxidases; other ligniolytic bacteria enzyme also contribute to delignification e.g. dye-decolorizing-type peroxidases; glutathione-dependent β-etherases and lignin-modifying laccases;*
4. *References* [127, 135, 136]*;*
5. *References* [127, 135, 137]*;*
6. *References* [137, 163-165]*.*

2.2.2 Aquatic biomass

Aquatic phototrophs, such as microalgae, macroalgae and seagrass, offer alternative resources to the terrestrial biomass. As summarised in Table 2, aquatic biomass demonstrates a range of favourable traits thus is in general considered as more environmentally sustainable but less economically feasible feedstock for biorenewable conversion compared with resources on lands [116]. Based on the economic viability comparison, future potential aquatic biomass resources are estimated as 515 EJ/yr globally (Figure 6), where four types of algae cultivation systems have been projected as the main contributors. Under elevated CO_2 concentration in future, aquatic macroautotrops i.e. macroalgae and seagrass are predicted to respond strongly with increased photosynthetic and carbon use efficiency, which are similar to the estimated trends for C3 higher plant species [166].

The term algae was used to refer to eukaryotic organisms either unicellular (microalgae) or multicellular (macroalgae). But this term often is expanded to include eukaryotic organisms and cyanobacteria and have been regarded as third or fourth-generation (3G or 4G) feedstock, gaining increasing research attentions recently. Algae are very diverse with over 40,000 species already identified [113, 148]. In general, algae contains lipids, proteins, and carbohydrates that can be converted and upgraded to a variety of bio-products (e.g. hydrogen, bio-methane, biodiesel, jet fuel, bioethanol), varying with the types and strains. An overview of the key algal taxonomic groups and their properties have been presented by Suganya et al. [148]; the strain-specific algal composition comparison demonstrates that the macro algae contains higher carbohydrates (16-56% dry basis) but much lower protein (5-21%) than microalgae (47-63% protein and 4-32% carbohydrates on dry basis).

As highlighted in Billion-ton report [147], driven by the difference in growth medium, water and resource demands, storage nutrient and water recycling, algae and terrestrial feedstock present different supply and geographical trends. Generally, algae use non-portable water, showing much lower solid concentration and higher (around 90%) nutrient and water recycling potential than terrestrial biomass; however, higher harvesting frequency and shorter storage duration can be expected for algae biomass. Currently, more than 90% of microalgae production globally are being used for nutritional products. The estimate of total microalgae biomass production is 15,000 tons/year, of which about two-thirds is Spirulina, one-fourth is Chlorella, and the rest is Duniella and Haematococcus [167]. Algae cultivation is dominated by open pond system (>95% of current microalgae biomass) whereas the scaling-up of photo bioreactor (a more productive and controllable cultivation systems) is constrained by the high operational and capital costs [167].

Microalgal strains have gathered special attention as promising aquatic resources for sustainable biorenewable production, particularly when compared to terrestrial plants[168-171]. The main advantages include high resource-utilisation efficiency, ability to compete against wild strains in open ponds, tolerance to a wide range of environmental conditions and seasonal variations, rapid growth and production cycles and high photosynthetic efficiency leading to high CO_2 sequestration capacity[172]. The overall solar energy conversion from resource to biofuel demonstrates that the solar energy return efficiency of microalgae is over 10 times higher than terrestrial crops[149, 173]. Such features could lead algal biorenewable production to be environmentally beneficial e.g. GHG mitigation potential and bioremediation potential.

Microalgal cultures can tolerate and capture substantially higher level of flue gas CO_2 emitted from industrial sources with a wide range of concentration from ambient (0.036%v/v) to extremely high (100% v/v) thus are considered as promising candidate carbon fixation technologies to mitigate CO_2[169, 174, 175]. Several studies have concluded that macroalgae as feedstock for CO_2 fixation and biofuel production could deliver overall energy benefits, depending on conversion technology choices [176-178]. Besides, the microalgal bioremediation of wastewater have been also examined. Previous research indicated that it could not only deliver environmental savings by avoiding artificial fertiliser inputs but also lead to reduced water demand [179-182]. Higher energy yields per unit land (about 30 times more oil) than terrestrial feedstock plus the avoidance of competition of productive land with food bring algae bioproduct systems with potential sustainability benefits [169, 183]. As demonstrated by Campbell et al. [184] and Clarens et al. [183], algae perform better than terrestrial crops on GHGs, land use and eutrophication for biofuel production.

Owing to the differed characteristics from terrestrial biomass, aquatic phototrophs offer promising resources for a wide range of conversion technologies particularly thermochemical and biochemical wet-route systems, which are energy-efficient for high moisture-content biomass. Besides, aquatic biomass offers desirable traits such as short storage duration and harvesting cycles, which are important design criteria for bioconversion process and network scheduling, logistics, value chain and system planning.

2.2.3 Waste biomass

Country-specific waste profiles vary but an increasing waste generation trend could be expected in response to expanding population and rapid urbanisation globally. Considerable amount of carbon-containing and nutrient-rich waste resources in solid (e.g. food waste), liquid (e.g. sewage sludge) and gas phases (e.g. carbon-containing greenhouse gases [138, 185]) are generated annually and could be converted via various routes to bioenergy or value-added bio-products. In the EU, the 900 million tonnes of waste paper, food and forestry and agricultural residues generated annually is predicated to result in sufficient cellulosic waste biomass for 16% of EU transport fuel by 2030[186]. In the UK, wastewater is estimated as 16 billion litre per day, which together with annual production of over 100 million tonnes of carbon-containing solid biowaste (e.g. BFMSW), above 14 million tonnes of forestry and agricultural residues and large amount of other waste provide significant opportunities [138].

A scenario-based study has estimated the global theoretical potential of agricultural and forestry residuals (i.e. the maximum available residue from crop harvest and round wood logging operation) as 140-170 EJ/year by 2100 [187]; if accounting for resource-competing sectors (e.g. livestock, traditional fuel use in developing regions), the 2100 available residue would come to 50EJ/year. Globally, one-third of food produced is lost or wasted every year, which is responsible for over 7% of the GHG emissions and the waste of $250km^3$ water (8.5% annual withdrawn), and 1.4 billion ha lands (28% of agricultural lands) [11]. This contributed to the global MSW generation. Out of 0.12-4.3 kg per day per capita global MSW, 59%-68% is organic fraction (e.g. food waste, paper waste and green waste), varying with the regions [140].

It is estimated to rise to 6.1 million ton/day by 2025 with over 65% as organic fraction [140]. A shift in the global MSW generation portfolio has been projected by World Bank, where the low-middle income countries (LMIC) are expected to contribute to 70% by 2025. Similar in wastewater treatment (WWT) sector, rapid increase in water consumption and discharge (1.7 times more rapidly than population growth) [141] and rising LMIC contribution have been observed. FAO AQUASTAT database showed that out of the currently global freshwater withdrawal (3928 km3/yr), 56% (2212 km^3) is released either as industrial WW, municipal WW or agricultural drainage, of which only 20% is treated via WWT [139, 141]. Due to the low development level of national WWT infrastructure (8-38% WWT in LMIC in contrast to 70% WWT in high-income countries [139]), LMIC represents future WW resource potential.

As highlighted in Table 2, due to waste sector complexity, chemical compositions vary with the waste type and show higher environmental, temporal and spatial variability in comparison with terrestrial and aquatic phototrophs. Cite compositional variation in livestock manure and food waste as examples. The former is highly influenced by the livestock species, diet patterns (e.g. forage and fodder feeding[188]), age groups, soil and climate [189]; whereas the latter is dependent on the regional human behaviours, seasonal variation in the diets and waste degradation [115, 190]. Sewage and livestock manure can be categorised as nutrient-rich waste while the high carbohydrate-containing waste category include starch-rich (e.g. food waste), lignocellulosic groups (e.g. agro and forest waste) and heterogeneous carbon-containing groups (e.g. wastewater). Compared with higher plant species (Figure 5), wastes in general represent wider variation in C:N ratio (7.9-398) and polysaccharide contents (cellulose and hemicellulose total contents ranging within 18-68.6). Under the paradigm shift from waste treatment to resource recovery via thermochemical or biochemical routes, environmental sustainability and resource-recovery efficiency are important key design criteria for system and process planning.

2.3 Biorenewable thermochemical conversion routes

Main technologies of advanced thermal chemical conversion of biomass include pyrolysis, gasification and hydrothermal liquefaction. Pyrolysis of biomass normally takes place at around 500 ºC in the absence of oxygen, to decompose biomass materials into char residue, liquid products and non-condensable gases[191]. Char and liquid oils are the main targeted products for the pyrolysis of biomass. Gasification of biomass happens at higher temperature (~900 ºC) in the presence of oxidant e.g. CO_2, H_2O or air, to produce synthetic gas (syngas) mainly including H_2 and CO[192]. Other gases such as CO_2, CH_4 and inert N_2 (if air is used for gasification) are present in the syngas. Another main method of thermal chemical processing of biomass is hydrothermal liquefaction (HTL)[193], which normally occurs at up to 400 ºC and 50 MPa, to convert biomass into mainly liquid products. HTL can use wet biomass without excess drying, which is very energy intensive. Therefore, microalgae are normally processed using hydrothermal liquefaction technology. The three main thermal chemical conversion technologies for biomass processing are summarized in **Error! Reference source not found.**, covering advantages, disadvantages, process conditions and products.

For the deployment of the advanced thermal chemical of biomass, many factors need to be considered, such as the type of feedstock[194], reactor design[195], process control, catalyst addition, product quality and market requirement, in addition to the impacts on environment and society.

Unlike coal, physical and chemical properties such as elemental compositions vary significantly between different biomass feedstock, which substantially affect the feedstock quality and processability. The change of moisture content, and the presence of ash/inorganic matters in biomass also make the operation of biomass conversion very challenging[196].

The technical aspects of torrefaction pre-treatment, pyrolysis, gasification and HTL are addressed in Supplementary Information SI-2 where lignocellulosic biomass [108, 197] is discussed in details. Typical properties of various lignocellulosic biomass feedstock are summarized in Table 3. Notably, the biomass component interaction (e.g. lignin acting as catalysts to promote secondary reactions for syngas production [198]), biomass screening based on chemical composition (e.g. cellulose) play significant roles in the design of thermal chemical processing. In Supplementary Information SI-2, the processes of individual component of lignocellulose using pyrolysis, gasification and HTL are discussed, which are followed by the interactions between the three biomass components; SI-2 covers the underlying mechanisms of biomass conversion, key parameters affecting technology performance and proximate and ultimate analyses. These offer fundamental knowledge underpinning process design and systems modelling to optimise the technology configuration.

Table 4 Overview of biomass pyrolysis, gasification and hydrothermal liquefaction

TECHNOLOGY	PROCESS CONDITIONS	PRODUCTS	ADVANTAGES	DISADVANTAGES	SUITABLE FEEDSTOCK
PYROLYSIS [191, 199, 200]	-Temperature: ~500ºC; -Pressure: normally atmospheric; -No added oxidants	-Char (~40 wt.%); -Liquid (~50wt.%); -Gas (~10wt.%)	-Can produce liquid fuels for transportation. -High value chemicals such as aromatics can be extracted from pyrolysis oil. -Biochar has a broad range of applications e.g. soil amendment	-Pyrolysis oil as the major liquid product is very complex, corrosive, non-stable, and high viscous	-Food waste, oil sludge. -Oil crops -Lignocellulosic feedstock (e.g. wheat straw, willow, miscanthus)
GASIFICATION [201-203]	-Temperature: ~800 ºC -Pressure: atmospheric (pressurised gasification also reported) -Air, steam or CO_2 used as gasification agent (air is normally used)	-Char (~5 wt.%, depends on the ash content); -Liquid (~5 wt.%) - Gas (~90wt.%)	-Can produce high value syngas used for the production of energy, power, and synthetic liquid fuels	-Tar production from biomass gasification significantly reduces the development of biomass gasification. -Tar can condense and block pipes and downstream facilities	-Lignocellulosic feedstock (e.g. wheat straw, willow, miscanthus) -Sewage sludge
HTL [193, 197]	-Temperature: 100-400 ºC -Pressure: up to 50 MPa. -Alkali slats used as homogeneous catalysts	- Liquid (up to 60 wt.%) -Char (~30 wt.%) -Gas (~10 wt.%)	-Can handling biomass with relatively high moisture content. -Can produce oil with relative low oxygen content compared with fast pyrolysis	- Energy intensive, high pressure operation increases equipment material costing and maintenance	-Aquatic phototrophs e.g. microalgae, macroalgae and seagrass. -Sewage sludge

2.4 Biorenewable chemical and biochemical conversion routes

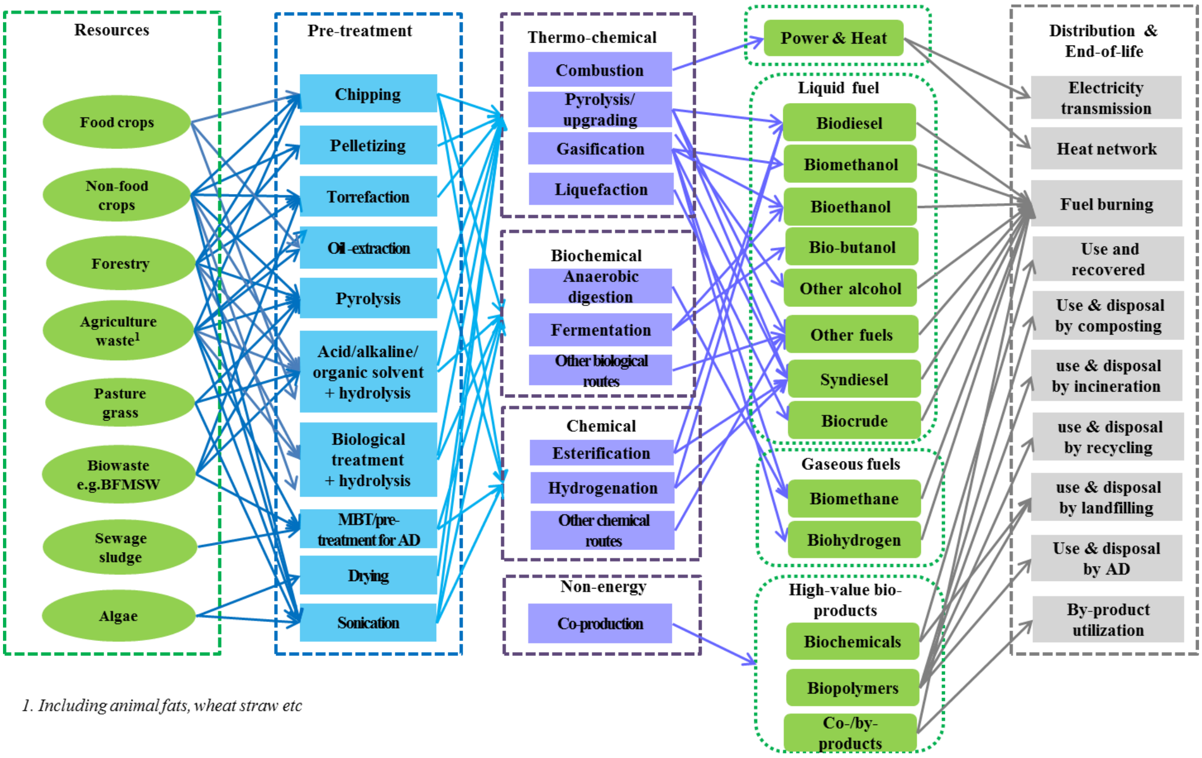
Main technologies for advanced chemical and biochemical routes include acid, alkali and bio-catalytic conversion. As the example given in Figure 7, many potential chemical and biochemical pathways can be integrated to transform different resources into value-added products. This section main discusses conversion of lignocellulosic biomass. Cellulose-first biorefining represents the most widespread technologies to convert structural carbohyrates of lignocellulosic biomass into biofuels and bio-chemicals (e.g. fermentable sugars). Such cellulose biorefining strategy separates lignin polymers from the plant tissues via lignocellulosic delignification and uses lignin as a waste product or low-value energy fuel. Alternatively, lignin first biorefining has also been proposed [204, 205], where different types of lignin can be processed to generate useful products. Notably, the lignin composition, structural complexity and reactivity not only vary with lignocellulosic plant species and genotypes but mainly depend on upstream processing technologies and sectors (e.g. kraft lignin from paper industry, organosolv lignin from bioethanol refinery, soda lignin from industry process)[206].

This section mainly focuses on cellulose first biorefining, where the fractionation pre-treatment can be grouped as chemical (e.g. alkali, acid, ionic liquid) pretreatment, thermal (e.g. steam), biological and physiochemical methods (e.g. mechanochemical). Extensive research have been published on pretreatment technologies; detailed technology comparison can be found in comprehensive reviews e.g. publications by Aditiya et al., [207], Kumar et al., [208], Zabed et al., [209] and Sivagurunathan et al., [210]. As summarised in Table 5, overall, chemical routes render effective fractionation, however bring design challenges e.g. solvent recycling, reactor anti-corrosion. Physio-chemical or chemical routes may lead to cost-effective solvent-free but energy-intensive solutions. Despite the advantages of low-energy demand and effective lignin depolymerisation, biological routes might be challenged by low reaction rate and inhibitor generation issues.

At conversion stage, enzymatic and acid hydrolysis are the mostly adopted technologies to derive fermentable monosaccharides from long chain of carbohydrate. This stage is critical since the quality of hydrolysate affects the subsequent treatment e.g. fermentation processes. In contrast to acid catalyst, enzyme is effective at a moderate condition hence leads to less capital investment; however, the production cost of enzyme has been acknowledged as barrier to enzymatic hydrolysis commercialisation[211]. Lignocellulosic hydrolysis catalysed by acids and enzymes have been covered in previous reviews [127, 211, 212]. Cellulase and xylanase are the mostly adopted enzymes to degrade cellulose and xylan (main compound forming hemicellulose) respectively; their mechanisms are discussed by Aditiya et al., [207]. Notably, enzymes play significant roles in industrial biotechnologies for biorenewable production. In addition to the common sugars abundantly occurring in nature (d-glucose, d-fructose, d-galactose, d-mannose, d-ribose, d-xylose, and l-arabinose), other rare monosaccharides and sugar alcohols (e.g. xylitol, mannitol, erythritol as sugar substitutes) can also be produced at enzyme-catalytic reaction (e.g. oxidization reduction, epimerization) [213]. Such enzymatic production of value-added biorenwables have caused increasing research attentions [213, 214].

Fermentation underpinned by enzyme actions to convert biomass to value-added products is of particular interests for biorefinery manufacturing. The 14 top chemical list recommended by US Department of Energy (DOE) [215] has positioned the fermentation as the fundamental component of biorefinery. In addition to alcohol commodities (e.g. bioethanol, sorbitol, xylitol), DOE highlighted a range of chemicals converted from carbohydrates through advanced fermentation processes - heterocyclic compounds (e.g. furfural, HMF), organic acids (e.g. lactic acid, succinic acid, HPA, levulinic acid), isoprene, glycerol and fermentation derivatives (e.g. 1,3-propanediol). The emerging role of fermentation in carbohydrate biorefinery is reconfirmed by the UKBiochem10 report [216], where 6 organic acids and 4 other building blocks are of commercial values. In addition, fermentation underpins the future food industries notably the new protein sources. Mycoprotein [217, 218], which has been developed through 3000 strain screening and commercialised since 1985, represents a successful case of continuous fermentation technology for food manufacturing (meat protein substitute) [219]. In addition, other bacteria, yeast fungi and algae strains for single cell protein (SCP) production have emerged since 1950s [220]. A review by Bogdahn [221] provides a comprehensive view of SCP producing strains, which is followed by a review on SCP landscape and patents published by Hakkinen et al [222].

Interestingly, extensive research [223-229] has been also performed on fermentation integration with thermochemical routes to form value-added bioproducts e.g. syngas fermentation [230].



1. Including animal fats, wheat straw etc

Figure 7 Pre-treatment and conversion pathways for biorenewable production

Table 5 Technology overview for biochemical and chemical routes

TECHNOLOGY	CRITICAL FACTORS	CATALYST /PRODUCTS	ADVANTAGES	DISADVANTAGES	REFERENCES
PRETREATMENT					
ALKALI	Reaction time, alkali loading	Alkali such as NaOH, Ca(OH)$_2$, NH$_3$ Products- Fractionated biomass	Low temperature, removal of lignin and part of hemicellulose	Low digestibility in softwood; water-demanding; pH adjustment needed	231-233
ACID	Acid concentration, temperature	Acid catalyst e.g. H_2SO_4, SO_2, HCl, H_3PO_4 Products- Fractionated biomass	Short retention time, effective lignin removal	Corrosive formation of inhibitors at low pH; formation of inhibitory by-products	234, 235
MECHANOCHEMICAL/MECHANOCATALYTIC TREATMENT	Ball-milling time, chemical/biomass ratio, temperature,	Metallic catalyst; organic solvent Products- Fractionated biomass	Effective fractionation,	Energy-intensive	136, 236
IONIC LIQUID	Anion and cation liquid composition, temperature,	Ionic liquid typically composed of large organic cations	low temperature, good selectivity	Cost vary; lack of commercial technology for ionic liquid	237-239

	retention time, biomass loading and particle size	and small inorganic anions	and low degradation of desirable products; no toxic gas; simultaneous dissolved lignin and carbohydrates; positive effects on enzyme activity	removal and recovery	
STEAM, SUBCRITICAL WATER	Temperature, pressure	Steam	Cost effective and chemical-free	High-energy inputs, high water demand	240, 241
BIOLOGICAL	Microbial strain screening	Enzyme from bacteria, fungi and actinomycetes.	Lignin degradation, energy-efficient, chemical free	Slow reaction time, inhibition effects	232, 242-245
CONVERSION					
ENZYMATIC HYDROLYSIS	Enzyme activity, stability and loading, residence time, composition and structure of biomass, particle size and porosity	Enzyme or acid as catalysts. Products -glucose, xylose, mannose, galactose, arabinose, lignin, cellulose nanofibrils	Good selectivity, effective degradation of cellulose and hemicellulose	Sensitive to inhibitors, high cost hindering commercialisation	207, 246, 247
ACID HYDROLYSIS	Acid loading,		Low cost; depolymerisation of cellulose and hemicellulose	Corrosion, acid recycling, high temperature; sugar degradation to form inhibitor	232
FERMENTATION TO GASEOUS FUELS	Fermenter type, residence time and temperature	Products - biomethane, hydrogen	Cost-effective; waste recovery for H_2 economy	Inhibitor formation and effects on microbial activity	208, 248, 249
FERMENTATION TO LIQUID FUELS	Fermentation reactors e.g. submerged and solid state fermentation; microbial strain	Products - bioethanol, biobutanol, hydrocarbon	Cost-effective Easy blend with petroleum fuels. Liquid biofuels with low requirements on fuel infrastructure change	Inhibitor effects on microbial activity; energy-intensive separation	232, 246, 250-252

FERMENTATION TO PLATFORM CHEMICALS	microbial strain; technology integration	Products – US Department of Energy top 10 +4 chemicals [215, 253] UK LBnet top 10 chemicals [216]	Integration with wide chemical, thermochemical routes; platform chemical and energy co-generation	Lack of mature technology for commercialisation	[230, 254]
FERMENTATION TO SINGLE CELL PROTEIN	microbial strain screening	Products – meat protein substitute; feed protein	Potential to bridge protein deficiency; environmentally sustainable protein option	Current food single cell protein depends on sugar derived from food crops [255].	[217, 220, 221, 256, 257]
TRANSESTERIFICATION	Biocatalyst and organic solvent addition	Biocatalysts e.g. lipase Products – Biodiesel and glycerol	Glycerol as value-added commodity	Critical factor is biocatalyst costs	[223, 258-260]

2.5 Biorenewable system complexity

Analysing from whole system perspectives, a considerable number of bioproduct value chains are involved in biorenewable systems. Value chains are composed of a full set of functional value-adding activities, incorporating biological renewable or waste resources, refinery processes and technologies (sections 2.3 and 2.4) that produce and distribute biorenewable commodities. Underpinned by biorenewable value chains, bioeconomy featuring biogenic carbon cycling, is circular by nature in contrast to the linear fossil-based economy. At upstream stages in biorenewable value chains, phototrophs and the related terrestrial and aquatic ecosystems represent potential carbon sinks for CO_2 capture and storage (as reflected by CUE in Table 2). At downstream stages, the carbon sequestered into the biomass is either fixed or cycled back to natural or built environments after conversion and use of bio-renewable products. In the case of bio-waste derived biorenewables, an infinite closed-loop carbon circular system could be theoretically formed. Thus resource-circular biorenrewable manufacturing underpinned by a sustainable nexus of resource-biorenewable-waste, if fully realised, will signal the bio-sectors transformation. Despite the science and engineering advances, tackling the complexity in the biorenrewable systems provides significant challenges. Below the biorenewable derived from terrestrial biomass is given as an example to highlight the challenges-

- Analysing biorenewable system complexity, the plant-environment interaction is driven by photosynthesis and biogeochemical cycles (defined as the pathways, by which chemical substances and elements move through the biosphere and physical environment of the Earth); whereas agriculture and refinery manufacturing are interconnected. As demonstrated in Figure 2, biorenewable are interdependent on natural capital (land, water, air) and built environmental resources (e.g. energy generation) due to its origin from biological renewable resources. Thus, different biorenewable sectors e.g. food and biochemical compete on the same natural capital and built resources, leading to demand stress.
- Biorenewable systems are not only regulated by environmental variability but also constrained by planetary boundaries (e.g. climate change, global freshwater use and land use boundaries [8]). As addressed in Section 2.1, the interaction between living organisms including plant species and agro-ecosystem functions are underpinned by photosynthesis, which is driven by light energy to convert CO_2 and H_2O into metabolites and O_2. C3 (e.g. wheat, willow, poplar), C4 plants (e.g. maize, sugarcane, miscanthus) have been the research focus as food and

lignocellulosic resources. Their photosynthetic reactions and biochemical regulation differ significantly. Not only regulated by plant internal physiological traits and metabolism pathways, their photosynthetic efficiencies and N update are also influenced by a range of external environmental drivers (e.g. soil, atmospheric CO_2 levels [25], water stress and temperature[19]) at spatial scales. At upstream stages, plant biomass production and chemical composition vary significantly with plant species and also show spatial-temporal variation and uncertainties, which affect downstream bioproduct manufacturing. Further, the biorenewable systems are constrained by land and water resource availability under ongoing environmental change as well as other planetary boundaries (e.g. stratospheric ozone depletion; ocean acidification [8]). Thereby, it is important to address interdependency of natural resources, biorenewable and environment while analysing biorenwable systems.

- Biorenewable systems consist of subsystems across temporal/spatial scales including natural capital resources (e.g. land, water and air), agro-ecosystems, refinery manufacturing, waste and pollutant fate and treatment, transport and network. Subsystems in particular those across different biorenewable value chains often are regarded as disconnected. Take lignocellulosic conversion as an example. A considerable amount of empirical research has been published on conversion technologies for lignocellulosic monosaccharides. Such empirical advances represent fragmented subsystems, which are discounted from the value chains of food and feed production (e.g. microbial protein). However, these sub-systems are interlinked by underlying carbon, nitrogen (C/N) cycles and resource circulation including biogeochemical cycles, water cycles, resource conversion and waste recovery. To unlock the subsystem fragments and enhance resource efficiency across renewable value chains, advanced whole system modelling offers an approach to push the research frontier on biorenewable systems design.
- Across the biorenewable value chains, different decision criteria and spaces are concerned. Figure 2 highlights considerable numbers of potential pathways (value chains) interconnecting biomass, conversion technologies and final biorenewable vectors. Across biorenewable value chains, multi-groups of interactive stakeholders are involved in the decision-making. Figure 8 generalises a sector-independent stakeholder map - feedstock and resource providers, existing bioproduct manufacturers, new biorenewable developers and operators, distribution centres, end-users, governmental agencies, policy makers and regulators and finance systems, thereby leading to diverse decision spaces. To achieve the new biorenewable technology deployment, it is essential to consider the entire value chains but also the interaction of different stakeholder groups with conflicting decision criteria.
- Biorenewable system development under Fourth Industrial Revolution (so called Industry 4.0) vision [261] represents an opportunity for bio-sectors transformation. Creation of intelligent biorenewable sectors and overcoming data barriers would not have been possible prior to Industry 4.0 [261]. Industry 4.0 envisages agriculture and manufacturing, where resources, bio-products and machines are all connected via the internet to achieve smart collection and analyses of real-time data and coordinated processes. Under this vision, emerging digital technologies and data advances (e.g. smart machinery, remote sensing) provide tremendous opportunities for biorenewable systems - enabling coordinated agriculture and manufacturing systems and bringing real-time data and information to precision decisions. Such advances also demand responsive decision-making, which requires a significantly reduced decision time with a trade-off with solution optimality.

Overall, terrestrial, aquatic biomass and waste resources can be converted into value-added biorenewables, which can be regarded as highly complex systems of flows and processes that are subject to nonlinearity, sensitivity and uncertainty. Biorenewables involve a range of conflicting and interacting issues such as sub-system interdependency, plant-soil-climate interaction, resource-competition, trade-offs between sustainability criteria, the interaction of bio-renewables with the evolving energy, water and waste sectors. It is essential to apply a whole systems approach and resilient and sustainable thinking [262] to biorenewable design in order to increase the overall capacity for tackling environmental stresses or socio-economic changes over the coming decades. Not only are sustainable resource management strategies for safeguarding agro-ecosystems necessary, but also biorefinery design needs to consider sustainability and resilience criteria in a spatial-temporal transition context. To advance understanding of biorenewables and inform robust solutions, a unifying modelling approach to account for varied nonlinearity and sensitivity of different computational methods is necessary.

Despite the clear importance, development and applications of advanced modelling tools to transform isolated subsystems to a performance-maximised biorenewable cluster with interconnected smart machinery and real-time data analyses remains unexplored. Digital technologies and data advances have the potential to bring improved responsiveness and flexibility, enhanced collaboration across supply chains for identifying and analysing resources and bio-products, and impact new biorenewable cluster creation. Beyond the state-of-the-art, an emerging research frontier is to bring data advances into responsive yet precision decision-making for the multi-scale decision spaces across biorenewable systems. Modelling research advances will be discussed in the section 3.

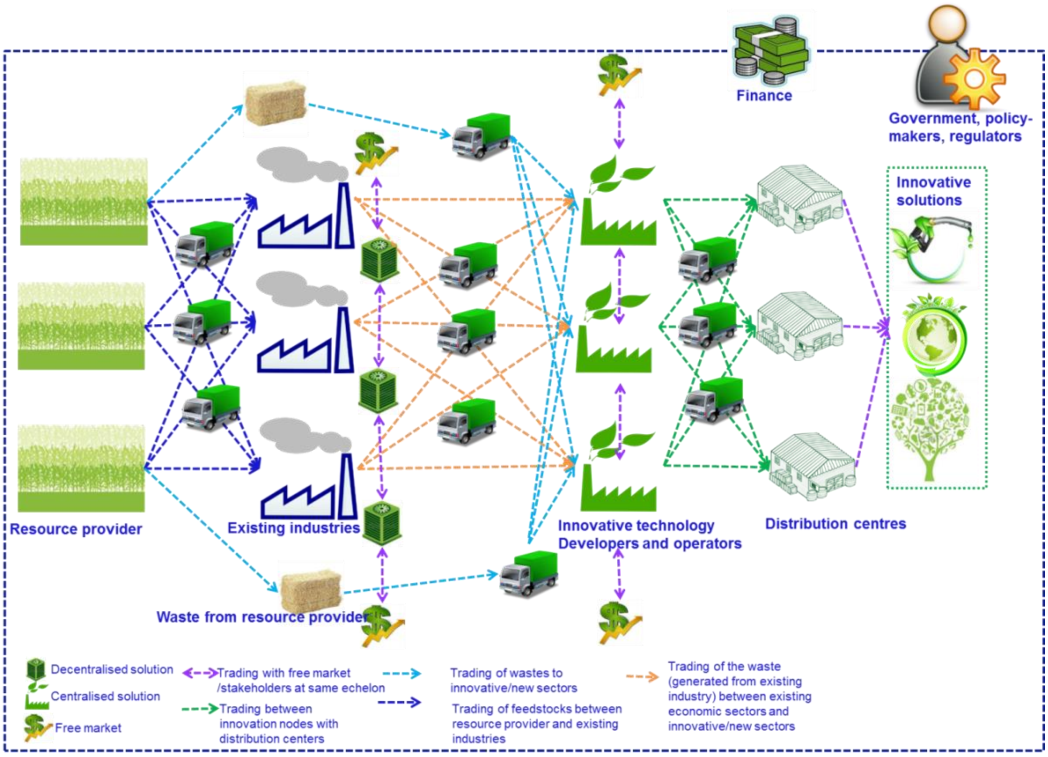


Figure 8 Stakeholder map for innovative biorenewable systems under circular bio-economy

3 Multi-scale biorenewable systems modelling

The biosector transformation calls for leading-edge research on multi-scale system modelling, which tackles the biorenewable complexity across scales and enables the optimal design of resource-circular manufacturing systems by capturing the interdependencies across resource-biorenewable-waste nexus. Through comprehensive review of state-of-the-art computational methods, this section highlights the modelling gaps and future research frontiers to address biorenewable complexity. Specifically, this section reviews metabolic and biogeochemical models, quantitative sustainable evaluation, spatial data analyses, process design and simulation and mathematical optimisation.

3.1 Metabolic and biogeochemical modelling

A multi-scale design by integrating modelling approaches with scientific innovation could not only lead to carbon closed-loop systems to fix CO_2 but also open up bioclusters to express our sustainable bioeconomy aspirations. This section provides an overview of multi-scale modelling approaches applied to the biomass systems.

3.1.1 Implementing system biology to understand global metabolism

Systems Biology is branch of science that looks at the global properties of a biological system being studied. Our knowledge of the foundations of living organisms, in terms of the components of cells, tissues, and organs has been expanded due to advances in high-throughput experimentation. Entire genomes of several organisms have now been sequenced and the gene expression profiles have been comprehensively generated [263]. Mass spectrometry-based protein surveys have quantified the global proteome [264] and the metabolome on cellular and organismal levels [265]. Advances in molecular and cell biology have provided information on how proteins are organised to orchestrate the functions of subcellular systems while physiology has shed further light on the complex functions of cells, tissues, and organ systems. This enormous amount of information at different scales of organisation can be used to obtain a new perspective that starts from genes and proteins, moves through subcellular interactions and pathways, and ends in the physiology of cells, tissues, and organ systems that determines the phenotype [266]. Systems Biology, therefore, offers an opportunity to study how the phenotype of an organism is generated from the genotype that is responding to its environment.

This combination of omics data and advances in computational analytical methods allows for a greater understanding of the data [266]. For the application of biotechnology, metabolism is the process in which photosynthetic organisms assimilate external substrates, such as CO_2 or acetate, into biomass rich in high value metabolites and understanding how metabolism can be directed to produce high quantities of high value compounds is key to a successful bioeconomy. A knowledge of metabolism is therefore invaluable in engineering microalgal strains optimised for efficient carbon uptake, assimilation and metabolism into high value bioproducts [267]. Computational models that describe metabolism can predict metabolism, whose results can be used to make novel model-driven hypothesis on how metabolism can be engineered to benefit the bioeconomy.

3.1.1.1 Metabolic modelling

Modelling metabolism can be undertaken using a variety of approaches, including kinetic, logic and stoichiometry-based methods [268]. Classical kinetic modelling approaches describe the rate of change in the concentration of a metabolite based on the kinetic properties of individual enzymes, using the corresponding experimentally derived parameters (e.g., rate constant, maximum reaction velocity and dissociation constants) [269]. Small metabolic networks (typically fewer than 50 reactions) can be modelled using kinetics [270]. The ability to model particular metabolic pathways such as the TCA cycle has given a greater understanding of how metabolic steps are regulated by enzymes that have the tightest control of the metabolic system [271]. The TCA cycle has also been modelled using differential equations, giving further information about alternative TCA cycles that could theoretically exist [272].

An example of a kinetic model of photosynthesis is e-photosynthesis, representing C3 photosynthesis as performed by wheat, rice and soybean crops [273]. This model consists of 50 differential rate equations that account for light absorption, hydrolysis, LEF accounted for NAPDH and ATP synthesis, along with CEF. Carbon fixation and assimilation up to sucrose synthesis was also represented in the model. The model was successful in accurately predicting qualitative and quantitative experimental data. Increases of photon flux led to the prediction of increased oxygen evolution, luminal pH and increased chlorophyll fluorescence, in line with experimental evidence [274-276]

Kinetic modelling is, however, limited to the current biochemical and experimental knowledge regarding the reactions being modelled. All reaction parameters, such as enzyme concentrations and their kinetic properties have to be accurately estimated in experimental conditions that mimic that of the cell to give meaningful results. Importantly, metabolic control analysis has taught us that control of a system is an inherent property of the global system, since metabolic control can be distributed among various metabolic steps [277]. Therefore, the greater the number of metabolic interactions, the greater the dispersal of metabolic regulation. By choosing to model selected pathways we are choosing to ignore any regulatory steps.

3.1.1.2 Simulating genome scale models using flux balance analysis

Metabolism is derived from the enzymes encoded by the genome; therefore, a complete knowledge of the genome would give a complete knowledge of metabolism for a given organism A GEnome scale Model (GEM) represents all known metabolic reactions in an organism and is reconstructed primarily from genomic information and the literature. Computational tools have been developed to analyse the system properties of GEMs. Flux Balance Analysis (FBA) is one such example that employs liner programming to optimise a defined biological objective (e.g., to maximise growth, or ATP production). In doing so, all input substrate fluxes and internal metabolic fluxes are directed to the objective reaction and in doing so, steady-state fluxes through all the reactions within the model are quantified. These quantified fluxes are thus deterministic upon available substrates and serve as metabolic predictions [278]. Knowledge of metabolite stoichiometry, metabolite and enzyme localisation, and biomass constituents are sufficient to generate predictions of metabolism, but integration of omic data that quantify the contributions made of each reaction within the GEM will give enhanced and reliable predictions of global metabolism [279]. By calculating steady-state metabolic fluxes through the GEM under specific conditions, i.e, mixotrophic algal growth on acetate versus phototrophic algal growth, the metabolic contributions of independent pathways can be observed and analysed with respect to the specified condition.

The underlying assumptions behind FBA is that metabolic pathways operate at steady state, and that biological systems have evolved to be as efficient as possible. The advantage behind this approach is that other kinetic parameters associated with the reactions can be ignored [280]. GEMs have proven useful for assessing the essentiality of metabolic steps [281], improving metabolic engineering strategies by simulating gene knockouts [282, 283], and for elucidating metabolism giving rise to observed physiological traits [284].

As represented in Figure 9, the first step of FBA is to mathematically represent a metabolic network in the form of a stoichiometric matrix (***S***), composed of rows of metabolites and columns of reactions. For each reaction within the matrix, metabolites that are consumed in that particular reaction are given a negative stoichiometric coefficient, whilst metabolic products are represented by a positive coefficient. The next step involves defining an objective function (Z) that is biologically relevant to the problem being studied. For predicting growth, for example, maximisation of biomass might be the best objective function, since biomass reactions contain all nucleic acids, proteins, lipids, etc., that are required for cell division. Another example of an objective function could be the optimal production of a target metabolite of interest or the minimisation of an expensive nutrient. The reaction that is deemed suitable as the objective reaction can either be maximised or minimised on the assumption that selective processes during evolution guide any systems towards an optimal state.

A further critical step involved with FBA is the application of constraints upon the matrix. Constraints are represented as upper and lower bounds for all reactions, which determine maximum and minimum allowable fluxes of reactions. For the constrained matrix (***S***), the overall reaction flux vector (v) in matrix ***S*** at steady state equals zero (***S*.**v = 0) ensuring a global mass balance through the matrix. It is for this reason why FBA is a constraint-based modelling approach.

The final step involves optimising the objective function using linear programming, which satisfies the steady state assumption. Metabolic networks are branched, and this branching allows for the possibility to generate several metabolic solutions that all satisfy the objective under the same constraints, because metabolic fluxes can be rerouted and/or distributed through each branching point.

The flux solutions are limited by the constraints imposed on the system, resulting in the allowable flux entering a theoretical phenotypic solution space. The greater the applied constraints, the tighter the available solution space will become with less. [285]. Analysis of the pathways carrying the greatest flux gives an indication of the metabolic pathways most likely to have been used in order to achieve a given objective.

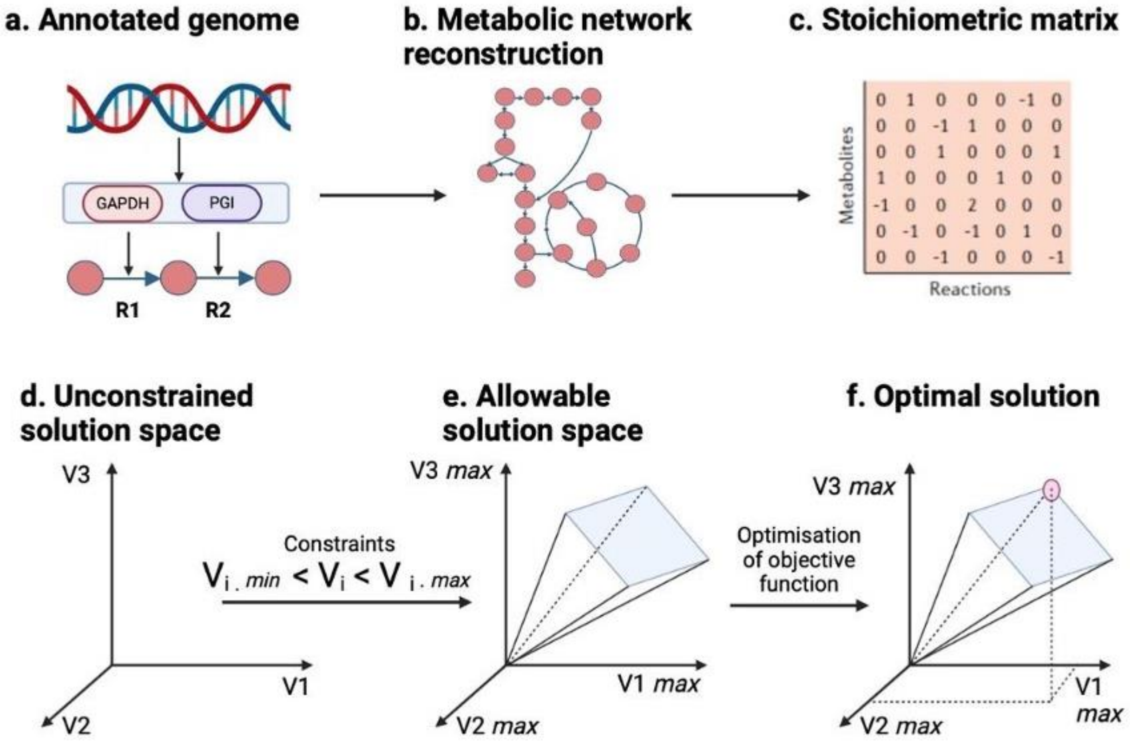


Figure 9 **Methodology of flux balance analysis to model metabolism**

(a) Metabolic genes from annotated genomes of interest and metabolic knowledge lead to global metabolic reactions. (b) Integration of all the metabolic reactions through shared metabolites results in the construction of a global metabolic network for the system of interest. (c) The metabolic network is converted into a stoichiometric matrix (S matrix), where columns represent reactions and rows represent metabolites and each entry represents the reaction coefficient of a particular metabolite in a reaction. Metabolites consumed by a reaction are given a negative coefficient, whereas positive coefficients are given to metabolites that are produced. (d) With the S matrix and the objective function of the model set as a system of linear equations, one can solve for the flux distributions throughout S. The phenotypic solution space (shaded blue rectangle) is where all possible solutions of flux distribution reside, and each axis represents the metabolic flux of a reaction in S. (e) Applying additional constraints will reduce the allowable solution space. (f) One or multiple optimal solutions can be found in the allowable solution space that optimises the objective function of the model (as represented by the pink dot) [278].

3.1.1.3 Flux Variability Analysis

In theory, the phenotypic solution space, (shaded blue in Figure 8) is not limited to single solution and so contains all possible flux combinations that the cell can use to sustain its objective function under the imposed constraints. FBA identifies one optimal solution in the presence of co-existing alternative optimal solutions. By using the principles that drive FBA whilst constraining the objective function at a given value, it is possible to calculate the range of possible minimal and maximal fluxes for each reaction in the network that give rise to the same optimal objective using a method called Flux Variability Analysis (FVA) [286]. As a result all alternative reactions that could carry a flux can be sought, giving rise to alternative pathways that still conform to the phenotypic phase plane.

A number of computational tools have been produced to analyse the fluxes resulting from a GEM using FBA. Becker et al., [287] developed a Constraint-Based Reconstruction and Analysis (COBRA) toolbox, a software package running from within the MATrix LABoratory (MATLAB) environment, and is also freely available for the Python and R environments [288, 289]. COBRA, and COBRApy allows for the quantitative prediction of both steady-state and dynamic optimal growth behaviour cellular flux and remains the most widely used method to model metabolism to date [287, 290].

3.1.1.4 Metabolic model advance of microbial cluster

GEMs have been constructed for many organisms including eukaryotic bacteria [291], cyanobacteria [292], yeast and photosynthetic organisms such as plants [293, 294] and microalgae [284, 295, 296]. Out of the various models of microalgae, it is the model organism *Chlamydomonas Reinhardtii* that has been most widely studied using metabolic modelling.

The first metabolic model of *C. reinhardtii* consisted of 484 reactions and 454 metabolites compartmentalised between the chloroplast, mitochondrion and cytosol [297]. The model was simulated to mimic phototrophic and mixotrophic growth at varying light levels using FBA. Phototrophic growth simulations predicted carbon fixation into the CBB cycle, and LEF of electrons through the photosynthetic reactions were predicted to produce NADPH. Mixotrophic simulations at periods of low light suggested an inhibition of carbon fixation into the CBB cycle because RuBisCO was inactive. At higher light levels, carbon fixation into the CBB was resumed by RuBisCO activity, and acetate was predicted to be assimilated into the glyoxylate cycle. Higher light levels also resulted in increased flux through LEF, producing more NAPDH than needed for biomass synthesis which then allowed for the fixation of carbon into the CBB. Despite qualitative and quantitative insights into carbon metabolism and light, the model did not contain CEF. In addition, the model contains an under representation of known reactions and metabolites as compared to other FBA models.

AlgaGEM, a genome-scale metabolic network model of *C. reinhardtii* represents a more complete GEM, accounting for 1725 reactions involving 1862 metabolites [284]. This model included the glyoxylate cycle within a microbody, in addition to cytoplasm, mitochondrion, chloroplast and nucleus compartments. AlgaGEM was constructed of the back of AraGEM, a GEM of *Arabidopsis thaliana* [293], and so 85% of reactions were identical between the two models. AlgaGEM was designed to investigate maximum hydrogen production in *C. reinhardtii* and was modelled under phototrophic, mixotrophic and heterotrophic simulations. Predictions from heterotrophic growth on acetate suggested acetate was assimilated into both the glyoxylate and TCA cycles. In this study, the CEF was associated with hydrogen production because mixotrophic growth predicted the activation of CEF, and resulted in a decrease of hydrogen production. The authors concluded that hydrogen itself is able to accept excess electrons when CEF is inhibited, providing a regulatory role of the reaction. This study has shown how predictive modelling can be used to address how physiological manipulations can give rise to emergent traits. However, the role of acetate and its effects on photosynthesis were not addressed.

*i*RC1080 is a more recent and dedicated metabolic model of *C.reinhardtii* that was developed to investigate light-driven metabolism [295]. This model accounts for 2190 reactions encoded by 1080 genes, 1068 metabolites and 10 compartments which included a glyoxysome. This model contained more than 32% of estimated genes with known metabolic functions, which remains a significant increase over previous reconstructions. Another key feature of this model is centrality of the chloroplast, accounting for over 30% of reactions in the model and displaying the importance of the chloroplast in carbon metabolism. Furthermore, the model was able to qualitatively predict correct oxygen evolution and growth rate with varying light sources and photon flux, thus displaying a greater coverage of the photosynthetic reactions. The *i*RC1080 model was then used to predict the flux of carbon metabolism and photosynthesis for mixotrophic and phototrophic conditions. The functioning of a CEF was predicted to be play an essential physiological role to assimilate acetate and to support a high biomass growth[298]. The results also suggested that acetate inhibits RuBisCO, which was recently confirmed [299]. Such modelling advances can help to inform the system design of various microalgal species as phototrophic microbial feedstock for enhanced biometabolite production.

Overall, omics-enabled metabolic modelling can advance the understanding of the phototrophic microbial cluster in biological CO_2 sequestration and carbon cycling in both terrestrial and aquatic ecosystems. Thereby, metabolic models not only can inform the large-scale biogeochemical cycles and ecosystem food webs but also can be integrated with first-principle modelling to explore the CO_2 conceptual refinery proposed by Mohan et al. [16]. By manipulating and designing versatile microbial consortia for carbon sequestration, CO_2 will be transformed from a GHG to a commodity, which can be metabolised to platform chemicals under circular bioeconomy. Driven by CO_2-underpinned resource-circular aspiration, the integrative modelling at the interface of Systems Biology and Process Systems Engineering to combine metabolic modelling with chemical process design and optimisation represents a future research frontier.

3.1.2 Biomass production modelling

3.1.2.1 Models for terrestrial higher plant biomass production

Photosynthesis is critical to the production of biomass, which underpins the complex interactions between organisms and ultimately, ecosystem functions. For higher plant species, photosynthesis is not only regulated by plant internal physiological traits and metabolism pathways, but is also affected by a range of biotic and abiotic environmental drivers such as climate, weather extremes, soil type and nutrient availability. The plant traits and environmental impacts are captured in bioenergy biomass crop production models such as MiscanFor for Miscanthus and C4 energy grasses [300], Forestgrowth–SRC for various species of woody trees used for short rotation coppicing (SRC) [301] or the ESC-CARBINE model for short rotation forestry [302, 303] , which is a combination of the CARBINE model [304] and the ESC model[305]. Environmental changes such as elevated atmospheric CO_2 levels, changing climate, and the increased intensity and frequency of extreme weather events could cause a widespread shift in photosynthetic patterns and regulators e.g. electron transport and RuBisCO capacity [306], where the response of different plant species may vary. With the rise in atmospheric CO_2 levels and associated global warming, RuBisCO capacity is expected to have a smaller role in limiting C3 photosynthesis [25] and species and genotypes with heat stability traits will be favoured for electron transport capacity [306]. Previous studies on the temperature response of photosynthesis suggested that C3 plants generally showed a greater propensity for temperature acclimation, C4 plants tend to be more adaptive to warm environments, whereas CAM species acclimate photosynthetic activities to temperature differently over day and night [19].

Photosynthetic efficiency dynamically adapts to a variety of internal physiological and external environmental factors, meaning that photosynthesis is heterogeneously distributed over leaves or organs over time. Such spatio-temporal variation has been reflected in previous modelling approaches, where regulatory properties, photosynthetic reactions and carbon assimilation potentials were simulated. Farquhar et *al.*[307] proposed a C3 leaf photosynthesis mode, capturing the enzyme kinetics and electron transport and photosynthetic responses to multiple and interactive environmental variables. This model was further adapted by Collatz et al. [308] to formulate a leaf biochemical-intercellular transport model for C4 plants, where photosynthesis was expressed as a function of temperature, intercellular CO_2 partial pressure and incident solar radiation. In previous research on C3 and C4 pathways, gross photosynthesis and carbon assimilation have been estimated not only *via* correlations with crop physiological factors e.g. leaf area, assimilate allocation [309], plant respiration [310], nitrogen uptake [311], but also *via* links with environmental drivers e.g. atmospheric CO_2 concentration [312], light interception [310] water and nutrient availability and stress, soil and ambient temperature [311, 313, 314]. Compared with C3 and C4 plants, CAM plants have received less systematic study. The net CO_2 uptake was often estimated based on the empirical environmental productivity index [315, 316]. A first order differential model proposed by Nungesser et al [317] formulated time-dependent concentration of metabolites as a function of atmospheric CO_2 concentration and light, which was further modified to include other factors, i.e. light intensity and temperature effects [317, 318]. This model was further adapted by Owen and Griffiths [319] which led to a system dynamic model integrating biological constants (e.g. enzyme kinetics) and capturing four distinct CAM cycle phases. Modelling efforts have been also made to correlate water availability to C assimilation [320] and coupling CAM photosynthesis with wider environmental parameters. Recent work by Bartlett et al. [321] proposed a dynamic model incorporating a CAM leaf photosynthesis model adapted from a C3 model [317], circadian C-flux dynamical model, stomatal conductance equation and soil-plant-atmosphere. Such photosynthesis models e.g. C3 model by

Farquhar et al. [307] have been widely used to model leaf biochemistry to canopy and ecosystem exchange in response to environmental change [322, 323] and constant/periodical environmental conditions [324].

Particularly, C3 and C4 photosynthesis models have been incorporated into site-scale crop-growth or large-scale vegetation models [325] e.g. GECROS [326], Agro-IBIS [327], WIMOVAC [328]. In the crop models, subtracting the plant respiration [310] from gross photosynthesis, the derived net C assimilation can be partitioned between leaf, stem, grain, shoot and root [311] to project biomass growth. In fact, crop growth are closely related to wider environmental processes e.g. soil biogeochemical processes and hydraulic dynamics, and such complexity can be captured by terrestrial biogeochemical models linking crop physiological processes and soil biogeochemistry [311]. Publically available and crop specific crop and biogeochemical models are summarized in Table 6, which have been applied to simulate the biomass and C/N cycle dynamics or combined with remote sensing for aspiration of precision farming[329, 330].

There are over 30 models [331, 332] that evaluate the carbon and nitrogen cycles and water flows that control the flows of nutrients in soil. These range from models that consider the decomposition of organic carbon in soils like the RothC[333] [334]and the cohort models developed by Bosatta and Ågren [335-341] and models that just consider the nitrogen cycle of nitrification/denitrification and plant uptake like Sundial [342] and hydrology models like SWAT [343] to models that include all processes like DayCent [344], ECOSSE [345, 346] and DNDC [347-350].

To take one model in more detail to understand how it evolved, DNDC is one of the most widely-used process-oriented biogeochemistry models and has been validated worldwide [351-360]. The DNDC (DeNitrification-DeComposition) model was first proposed by Li et al. [347]; over two-decade development, numerous changes have been implemented to DNDC model to bridge functional gaps and be adapted to region- or user-group specific versions UK-DNDC [354], DNDC-Europe [361] forest-DNDC, manure-DNDC [362]. A schematic family tree has been reviewed and presented by Gilhespy et al. [363]. DNDC embed biogeochemical processes (e.g., plant growth, organic matter decomposition, fermentation, ammonia volatilization, nitrification, denitrification) to compute transport and transformations in plant-soil ecosystems. Specifically, DNDC has two components – 1) soil climate, crop growth, and decomposition sub-models, converts primary drivers (e.g., climate, soil properties, vegetation, and anthropogenic activity) to soil environmental factors (e.g., temperature, moisture, pH, redox potential, and substrate concentration gradients); 2) nitrification, denitrification, and fermentation sub-models, simulates C and N transformations mediated by the soil microbes [361]. DNDC has been linked with economic model to simulate C N fluxes under the regional context of environmental and economic indicators [364]. Despite its original development for agricultural land and crop modelling (annual or perennial food crops), the plant growth sub-model was modified to enable DNDC to simulate the perennial plants (e.g. poplar) with woody stem or roots [361]. By linking with chemical engineering process design and life cycle assessment, DNDC has been applied to simulate biomass growth and carbon/nitrogen cycling in agro-ecosystems and their implications on bioproduct system sustainability [361, 365]. By adopting an integrated modelling approach, the performance of different species and genotypes in response to the future environmental changes can be projected and desirable traits can be highlighted that will pre-adapt species to future changes e.g. warmer, CO_2-enriched environments. Such modelling research can provide scientific evidences to inform empirical efforts (e.g. breeding and genetic engineering) to improve the performance-limiting traits and set the performance targets.

The biogeochemical processes and involved C/N cycles are visualised in Figure 10. The biogeochemical process based models have been used to understand the nitrogen and carbon cycles that are observed in field experiments using eddy covariance flux and chamber measurements to understand the interaction of these processes with climate and the soil environment for different land uses from arable [366], grassland [367, 368], forest and peatlands [369]. In addition using carbon and nitrogen isotope measurements to identify the pathways for N16 labelled nitrogen amendment to soil and their partition into plants and N and N_2O emissions. Similarly the fate of organic carbon additions to the soil have been modelled by tracking the radioisotopes of carbon C13 and also naturally occurring C12 and C14 isotopes, which occur in different proportions in C3 and C4 plants.

Coupling the biosphere modelling with atmospheric circulation models have attracted great research attention. Soil processes and plant growth cannot be considered in isolation so that there are several trials of coupling plant and soil processes models (called bottom up models) with atmospheric circulation models (top down models) to look at the feedback and interaction of the emissions of the biosphere and albedo it creates with the atmospheric processes such as JULES [370, 371] . This represents the subject of ongoing research and future directions.

3.1.2.2 Models for aquatic biomass production

Research on terrestrial agriculture is more advanced than aquatic biomass farming in general. Compared with terrestrial modelling advances, aquatic model development and validation face the challenges in measurements (e.g. primary production), remote-sensing and scaling-up as well as the limitations led by decoupled modelling approaches.

Systems approaches have played an important role in aquatic phototroph metabolism and ecosystems research e.g. the mathematical models developed based on first-principles for predicting the growth of open-pond microalgae in response to weather variability [372], computational fluid dynamic-based optimisation for algae growth simulation under photo bioreactors [373]. However, previous modelling efforts have mainly focused on monoculture metabolism at lab scale (e.g. photo bioreactor) rather than reflection of complexity in reality. The current dominant algal cultivation methods i.e. open pond system are highly susceptible to contamination where the dynamics of bacteria communities and their interaction with algal cultures are involved. To solve such complexity including the resource-competition, metabolism and related biogeochemistry trajectories of aquatic microbial ecosystems, a generalised optimisation model has been proposed based on the thermodynamic, kinetic and stoichiometric theories [374]. The models *via* parameterisations of aquatic ecosystem function primary production, nutrient recycling as a function of biotic/abiotic environmental parameters have been developed to determine the energy and nutrient and carbon mass flux [375]. Such a biogeochemical circulation approach was further incorporated into ecosystem models and combined with traits-based modelling which account for the bottom-up controls of phytoplankton community structure and composition as a consequence of ecological taxa selection [376]. Environmental Modelling Suite (EMS) presented by Australia's Commonwealth Science Industry and Research Organisation (CSIRO) is a good example, which formulates the traits and biogeography of aquatic macroautotrophs (macroalgae and seagrass) in response to bottom-up controls (light, nutrient, temperature) and project their biomass potentials and carbon cycles [377]. The EMS-CSIRO model considers two absorbance-distinct photopigments Chl *a* and photosynthetic xanthophyll but with simplified physiological process [377]. As pointed out by Schartau et al., [378], and Doney [379], most of these published models are unrealistically simplified, meanwhile challenged by spatial/temporal-dependence parameterisation and cross-validation issues, due to the limited observation data for scaling-up from laboratory to mesocosm experiments. Particularly, the underlying photosynthesis dynamics are often simplified by using 'black box' representations of organism eco-physiology e.g. parameterisation of a small number of traits for nutrient and light acquisition [380], photosynthetic efficiency normalised to pigment Chl *a* concentrations and aggregated species into model functional groups [378]. Moreover, models based on the empirical description of organism traits are considered to present great uncertainties in the projection power and process-based understanding of the future responses to new environmental conditions (e.g. climate change) beyond historical envelope[380].

Overall, the decoupling of phototroph metabolism traits from hydrodynamics, biochemical and sediment models in aquatic environments remains a research gap. The next generation models proposed by Mock et al. [380] and Welti et al. [381] could represent a research direction i.e. to adopt the process-based approaches across biochemistry, evolutionary ecology and integrate the interconnected omics data and environmental variables in food web ecosystem metabolism and aquatic biogeochemical modelling.

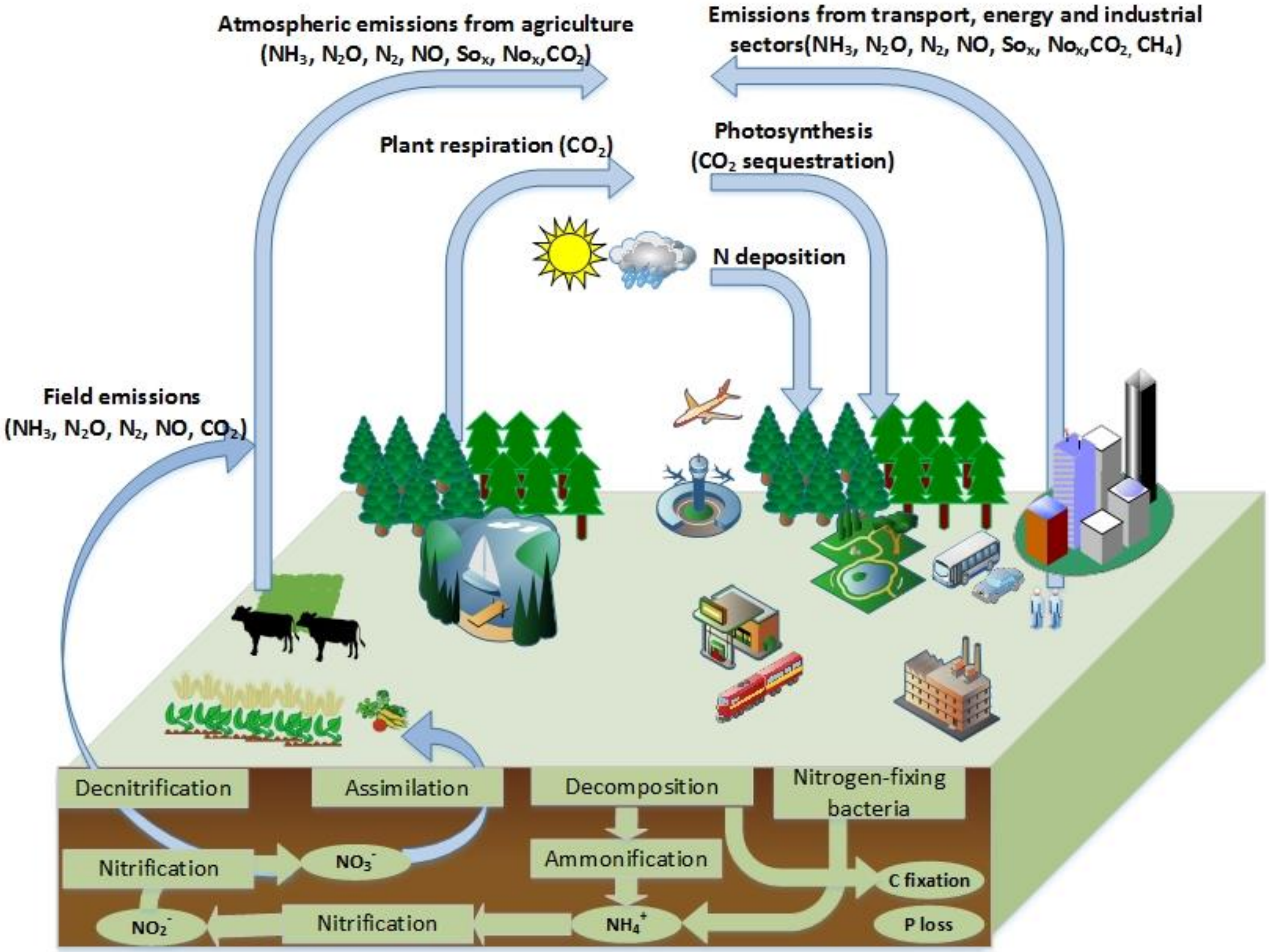


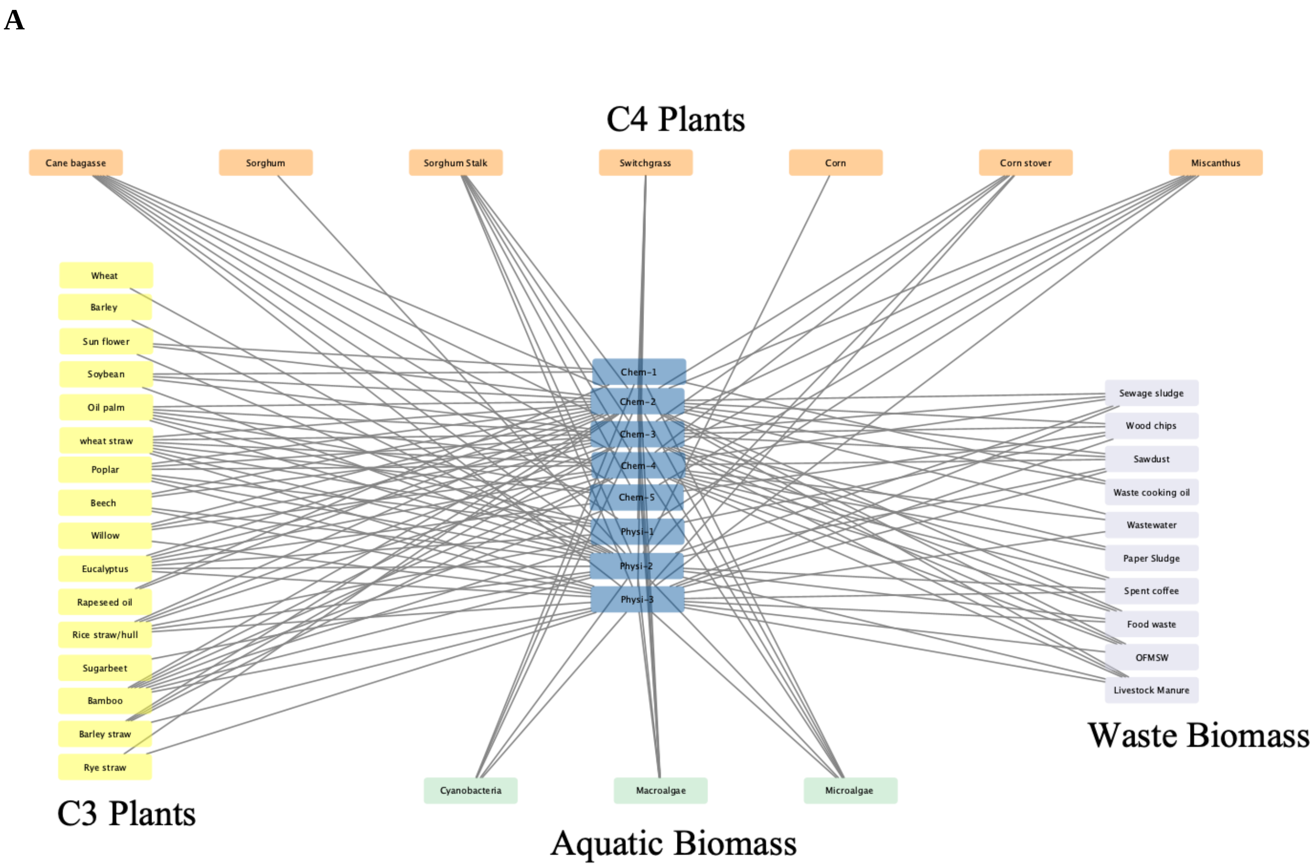
Figure 10 Biogeochemical cycles

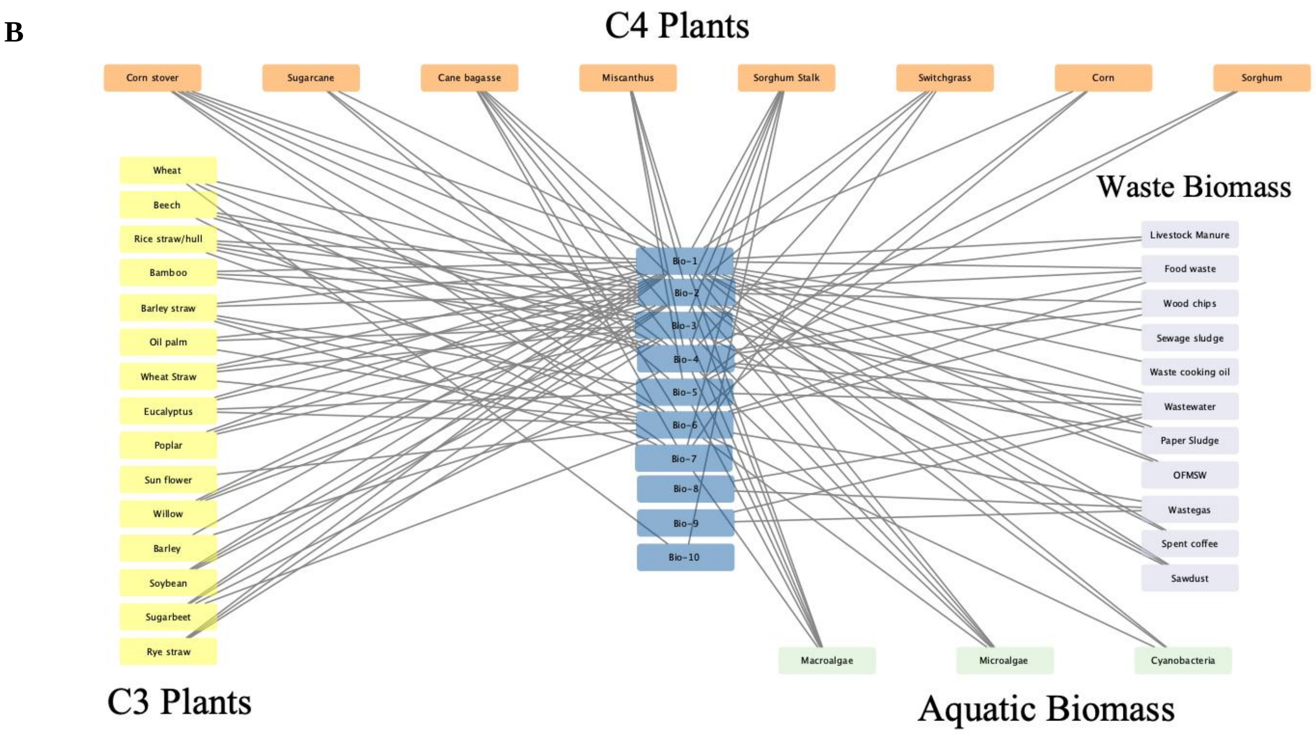
Table 6 Biogeochemical model overview

MODEL	PHOTOSYNTHESIS	TEMPORAL-SPATIAL SCALE	SUB-MODELS	ENVIRONMENTAL VARIABLES		BIOMASS		REFERENCE
				Weather [1]	**Soil [2]**	**Plant species**	**Parameter [3]**	
DAYCENT	Degree day model	Site/regional/global, Monthly or daily	Biomass decomposition nitrification denitrification methanogenesis soil climate	AT, SR, Pre, WS	Multilayer PH, B-Den, Or-C, S-Tex, Slop, In-N, WP, H-Con, Por	C3 and C4; terrestrial general	LAI, C-Par, C/N, WaD, N-Fix, ThD, Root, Op-T, FO-P, FO-T, FO-F, FO-I	[344, 382]
ECOSSE	Miami NPP model	Site/regional/global, Monthly or daily	Biomass decomposition nitrification denitrification methanogenesis soil climate	AT, SR, Pre, WS	Multilayer PH, B-Den, Or-C, S-Tex, Slop, In-N, WP, H-Con, Por	C3 and C4; terrestrial general	C Par C/N	[383]
DNDC	Degree day model	site/regional/global; julian days	soil climate, crop growth, decomposition, nitrification, denitrification, fermentation	AT, SR, Pre, WS	PH, B-Den, Or-C, S-Tex, Slop, In-N, WP, H-Con, Por	C3 and C4; terrestrial, crop specific	LAI, C-Par, C/N, WaD, N-Fix, ThD, Root, Op-T, FO-P, FO-T, FO-F, FO-I	[347-350]
MISCANFOR	Monteith – LAI – extinction coef – RUE modified for 40 áter 40 atura drought and nutrient stress	Site/regional,/global Monthly or daily	Biomass Decomposition soil wáter wáter use, LCA	AT, SR, Pre, ET, WS	PH, B-Den, Or-C, S-Tex, Slop, In-N, WP, FC, Por	C4 grasses and Wood SRC genotype specific	LAI, C-Par, C/N, WaD, N-Fix, ThD, Root, Op-T, FO-P, FO-F, FO-I RUE, WUE	[314]

FORESTGROWTH-SRC		Site/regional, (UK) Monthly or daily	Biomass soil 41áter soil wa	AT, SR, Pre, ET, WS	Multilayer PH, B-Den, Or-C, S-Tex, Slop, In-N, WP, H-Con, Por	Wood SRC genotype specific	LAI, C-Par, C/N, WaD, N-Fix, ThD, Root, Op-T, FO-P, FO-F, FO-I RUE, WUE	[301]
CARBINE-ESC	Annual timestep growth curves	Site/Regional Anual (UK)	Surface biomass	AT, SR, Pre, WS		Trees genotype specific	Par	[384]
SWAT	Degree days	Site/regional/global, Monthly or daily	Biomass nitrification Leaching soil climate Wáter erosion	AT, SR, Pre, ET, WS	Multilayer PH, B-Den, In-N, WP, H-Con, Por	Trees/grass/arable functional types	LAI Par, ThD C/N FO-I	[385]
PASIM	Leaf área and photsynthesis	Site/regional/global, Monthly or daily	Biomass decomposition nitrification denitrification methanogenesis Grazing soil climate	AT, SR, Pre, ET, WS	Multilayer PH, B-Den, Or-C, S-Tex, Slop, In-N, WP, H-Con, Por	Grass	LAI, C-Par, C/N, WaD, N-Fix, ThD, Op-T, FO-P, FO-F, FO-I RUE, WUE	[386-390]
ORCHIDEE	Leaf área and photsynthesis	Site/regional/global, Monthly or daily	Biomass decomposition nitrification denitrification methanogenesis? soil Climate feedback	AT, SR, Pre, ET, WS	Multilayer PH, B-Den, Or-C, S-Tex, Slop, In-N, WP, H-Con, Por	Trees/grass/arable functional types	LAI, C-Par, NPP N-Fix, WUE, Abido	[386]

1. *AT=ambient temperature; SR=solar radiation; Pre=precipitation; WS=wind speed;*
2. *B-Den=bulk density, Or-C=organic C; S-Tex= soil texture (silt/clay/sand); In-N=initial Nitrogen (*NO_3^-/NH_4^+*); WP=wilting point; FC=field capacity; H-Con=hydro-conductivity; Por=porosity*
3. *LAI=leaf area index; C-Par = carbon partitioning; C/N=biomass C/N ratio; WaD=water demand; N-Fix=N fixation index; ThD=Thermal degree days for maturity; Root=Maximum root depth; Op-T=optimum temperature; FO-P=field operation planting; FO-T=Tillage; FO-F=fertilization; FO-I=irrigation. WUE=water use efficiency*


A
C4 Plants
Cane bagasse
Sorghum
Sorghum Stalk
Switchgrass
Corn
Corn stover
Miscanthus
Wheat
Barley
Sun flower
Soybean
Oil palm
wheat straw
Poplar
Beech
Willow
Eucalyptus
Rapeseed oil
Rice straw/hull
Sugarbeet
Bamboo
Barley straw
Rye straw
C3 Plants
Chem-1
Chem-2
Chem-3
Chem-4
Chem-5
Physi-1
Physi-2
Physi-3
Sewage sludge
Wood chips
Sawdust
Waste cooking oil
Wastewater
Paper Sludge
Spent coffee
Food waste
OFMSW
Livestock Manure
Waste Biomass
Cyanobacteria
Macroalgae
Microalgae
Aquatic Biomass


B
C4 Plants
Corn stover
Sugarcane
Cane bagasse
Miscanthus
Sorghum Stalk
Switchgrass
Corn
Sorghum
Wheat
Beech
Rice straw/hull
Bamboo
Barley straw
Oil palm
Wheat Straw
Eucalyptus
Poplar
Sun flower
Willow
Barley
Soybean
Sugarbeet
Rye straw
C3 Plants
Bio-1
Bio-2
Bio-3
Bio-4
Bio-5
Bio-6
Bio-7
Bio-8
Bio-9
Bio-10
Waste Biomass
Livestock Manure
Food waste
Wood chips
Sewage sludge
Waste cooking oil
Wastewater
Paper Sludge
OFMSW
Wastegas
Spent coffee
Sawdust
Macroalgae
Microalgae
Cyanobacteria
Aquatic Biomass

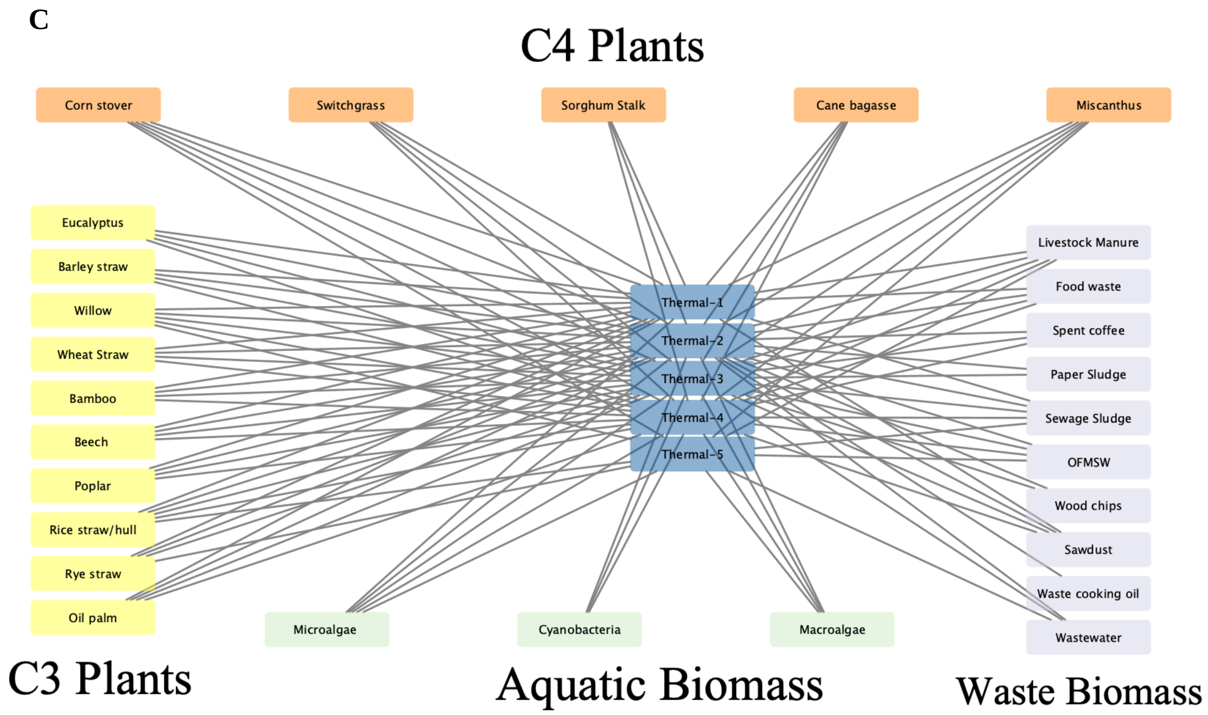
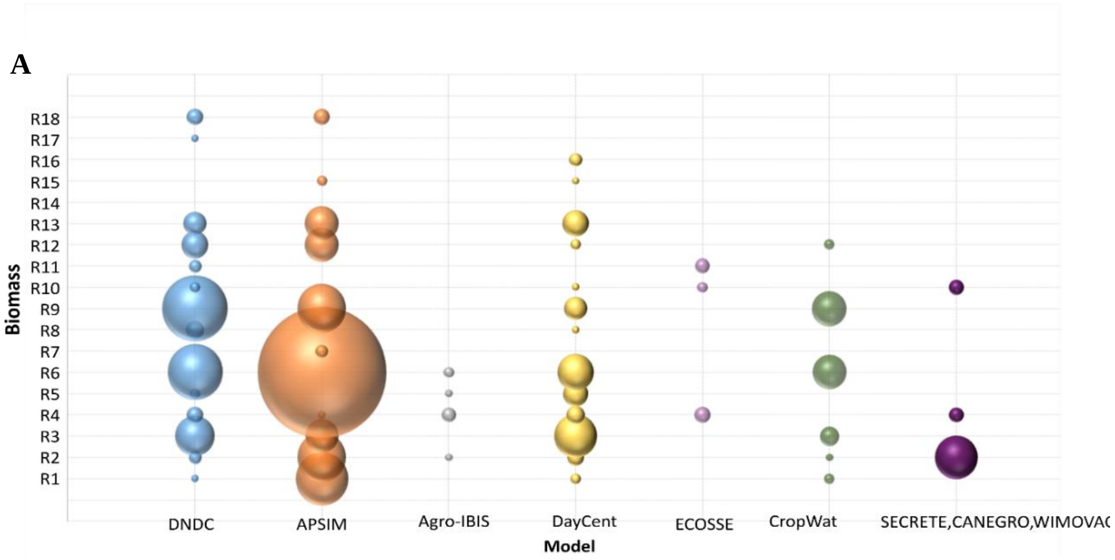


Figure 11 Overview of empirical research advances on biomass conversion *via* chemical/physical (A) biological/biochemical (B) and thermochemical (C) routes (Supplementary Information SI-3)

Grey links indicate the availability of technology routes. Chem-1 = Esterification; Chem-2 = Ionic liquid pre-treatment; Chem-3 = Acid treatment; Chem-4 = Alkaline pre-treatment; Chem-5 = Organic solvent; Physi-1 = Mechanochemical; Physi-2=Ultrasound; Physi-3=Microwave enhanced treatment; Thermal-1=Torrefaction; Thermal-2 = Pyrolysis; Thermal-3 = Gasification; Thermal-4 = Hydrothermal liquefaction; Thermal-5 = Hydrothermal carbonisation; Bio-1 = Anaerobic digestion; Bio-2 = Fermentation for bioethanol production; Bio-3 = Biobutanol fermentation; Bio-4 = Fermentation for lactic acid production; Bio-5 = Succinic acid bacteria fermentation; Bio-6 = Fungal fermentation for single cell protein production; Bio-7 = Acetone-butanol-ethanol fermentation; Bio-8 = Bioremediation by microbial cluster; Bio-9 = Phytoremediation by lignocellulosic plants; Bio-10 = Fermentation for hydrogen production.



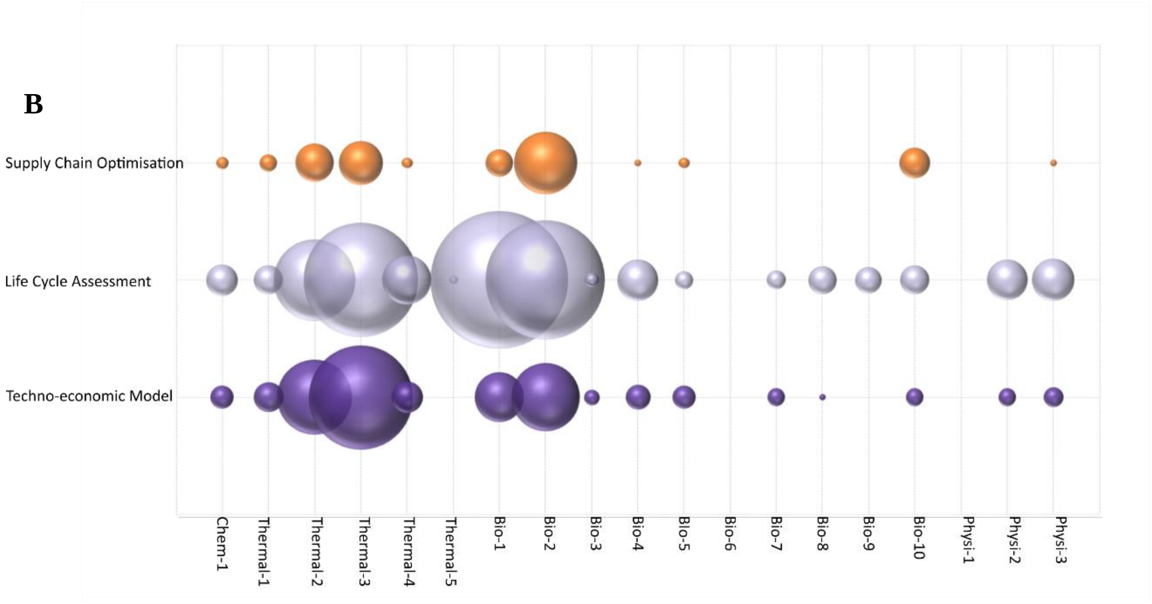


Figure 12 Biogeochemical modelling (A) and process simulation and supply chain optimisation research (B) (Supplementary Information SI-4) Bubble size indicates the number of studies.

R1 = Sorghum; R2 = Sugarcane; R3 = Corn; R4 = Miscanthus; R5 = Switchgrass; R6 = Wheat; R7 = Oil palm; R8 = Beech; R9 = Rice; R10 = Poplar; R11 = Willow; R12 = Barley; R13 = Soybean; R14 = Sugar beet; R15 = Rye; R16 = Sunflower; R17 = Bamboo; R18 = Eucalyptus.

Chem-1 = Esterification; Physi-1 = Mechanochemical; Physi-2 = Ultrasound; Physi-3 = Microwave enhanced treatment; Thermal-1 = Torrefaction; Thermal-2 = Pyrolysis; Thermal-3 = Gasification; Thermal-4 = Hydrothermal liquefaction; Thermal-5 = Hydrothermal carbonisation; Bio-1 = Anaerobic digestion; Bio-2 = Fermentation for bioethanol production; Bio-3 = Biobutanol fermentation; Bio-4 = Fermentation for lactic acid production; Bio-5 = Succinic acid bacteria fermentation; Bio-6 = Fungal fermentation for single cell protein production; Bio-7 = Acetone-butanol-ethanol fermentation; Bio-8 = Bioremediation by microbial cluster; Bio-9 = Phytoremediation by lignocellulosic plants; Bio-10 = Fermentation for hydrogen production.

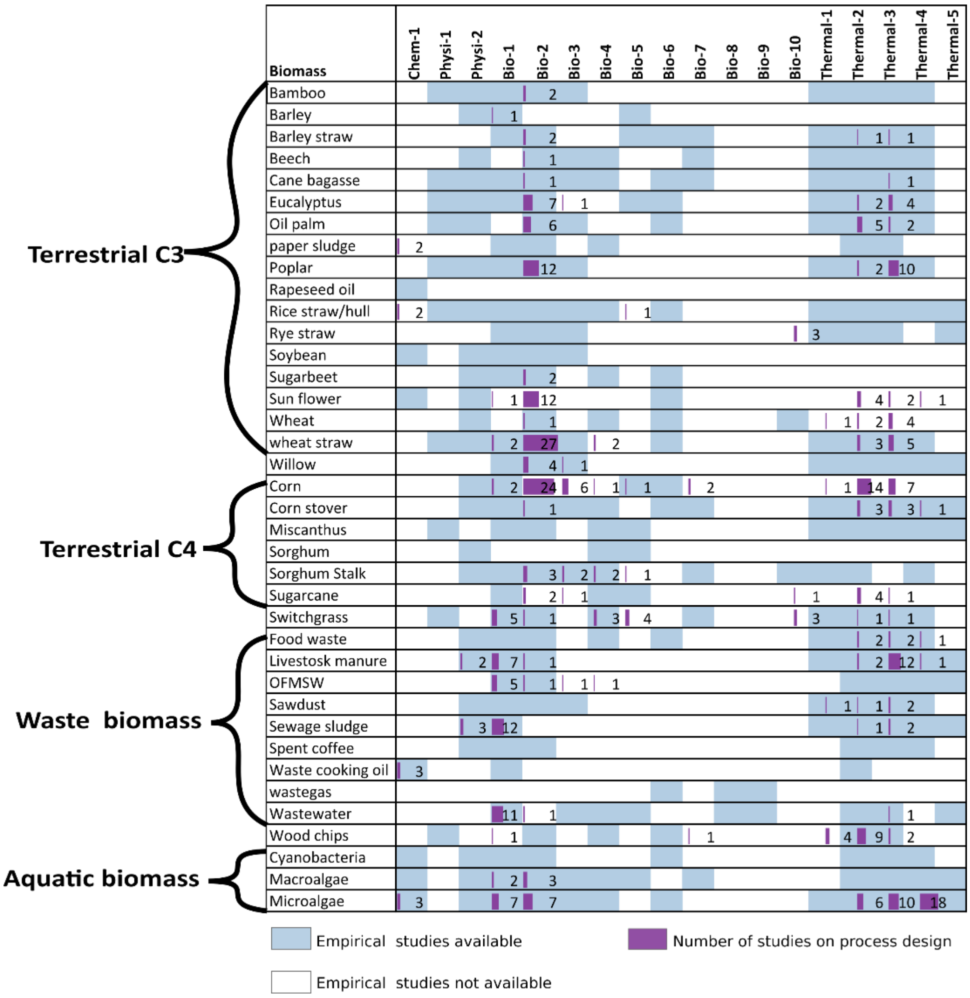


Figure 13 Empirical research vs. process design (Supplementary Information SI-3)

Chem-1 = Esterification; Physi-1 = Mechanochemical; Physi-2 = Ultrasound; Bio-1 = Anaerobic digestion; Bio-2 = Fermentation for bioethanol production; Bio-3 = Biobutanol fermentation; Bio-4 = Fermentation for lactic acid production; Bio-5 = Succinic acid bacteria fermentation; Bio-6 = Fungal fermentation for single cell protein production; Bio-7 = Acetone-butanol-ethanol fermentation; Bio-8 = Bioremediation by microbial cluster; Bio-9 = Phytoremediation by lignocellulosic plants; Bio-10 = Fermentation for hydrogen production. Thermal-1 = Torrefaction; Thermal-2 = Pyrolysis; Thermal-3 = Gasification; Thermal-4 = Hydrothermal liquefaction; Thermal-5 = Hydrothermal carbonisation.

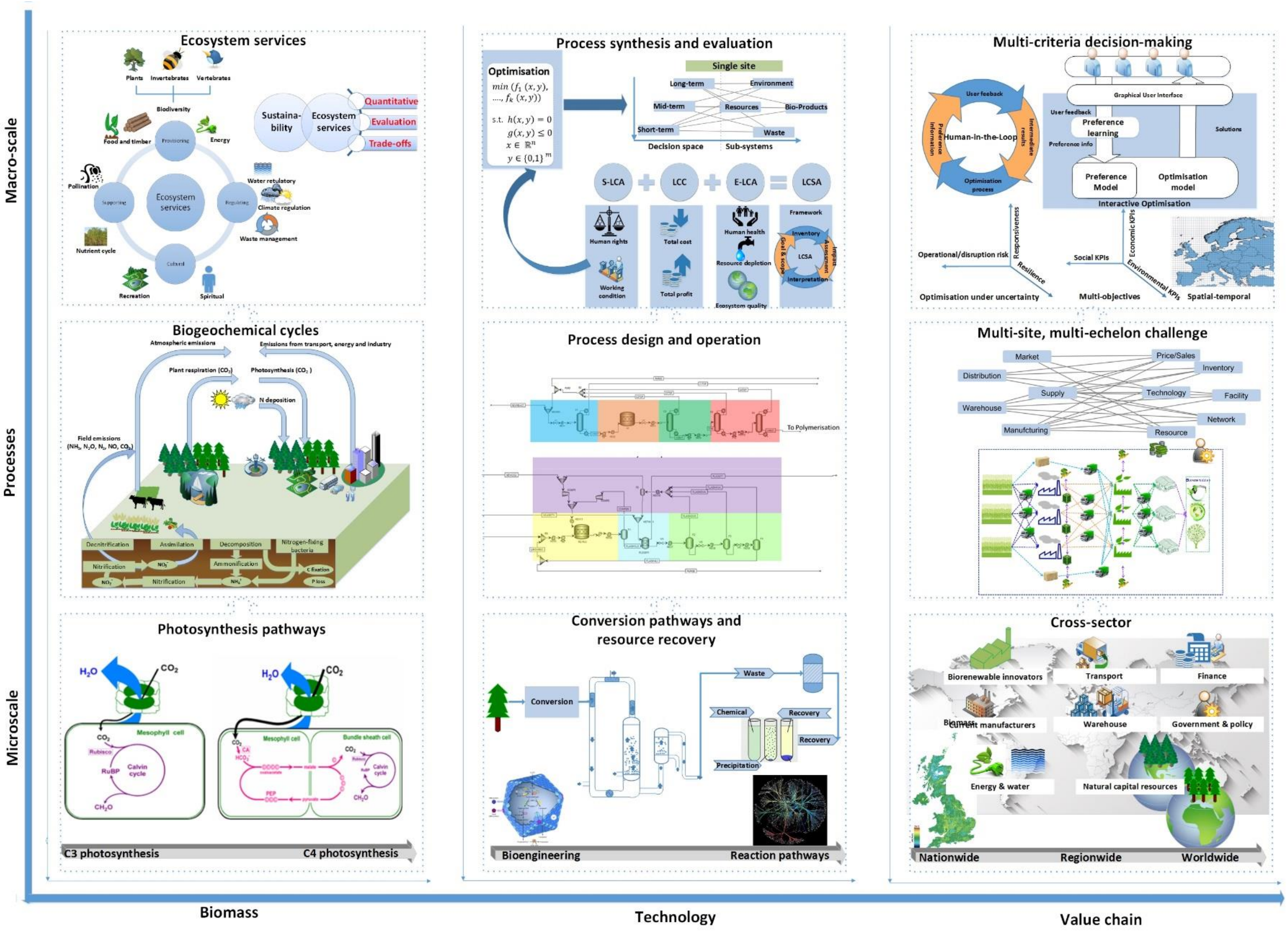


Figure 14 Multi-scale modelling framework

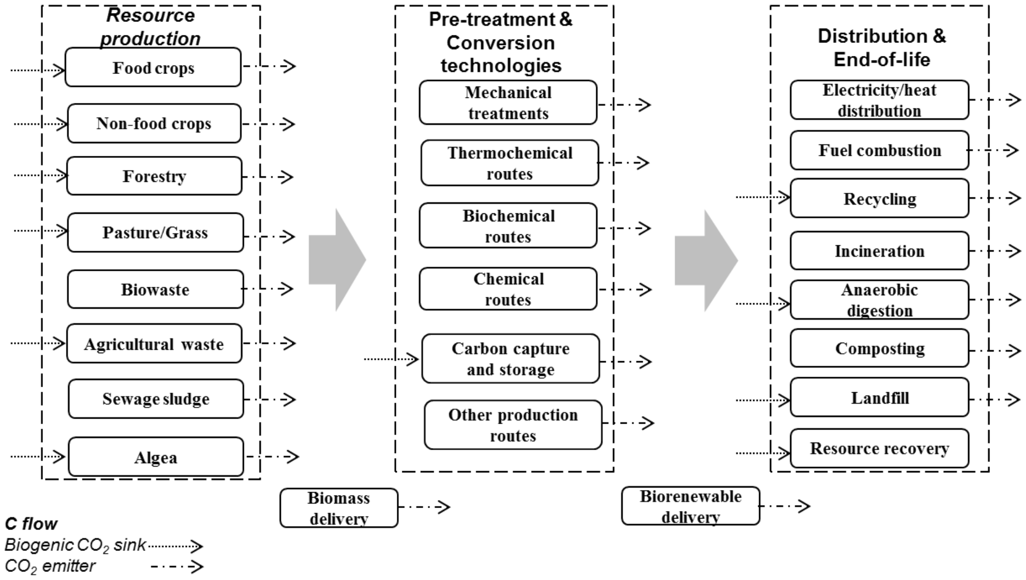


Figure 15 Biogenic carbon sinks and carbon emitters in biorenewable life cycle

3.2 Ecosystem services and sustainability evaluation

3.2.1 Ecosystem services

Landscapes generate a wide range of ecosystem services (ES) that provide benefits to human society [391, 392]. These services fall into four categories including - provisioning services such as biodiversity, food, materials and energy; regulating and supporting services such as climate and water regulation and waste recycling; and cultural services such as recreational value and symbolic meaning [188]. While the need of incorporating ES into decision-making at international, national and local levels is increasingly recognised [393, 394], and ecosystem accounting is increasing employed in research, policy and decision-making {Lange, 2022 #834}, the value of ES is often overlooked in natural capital resource planning [395], which underpins the development of the biorenewable sector. In the coming decades, changes in natural capital resources e.g. land use transitions could be expected to rise from the bio-renewable industry, which may occur against a backdrop of ongoing global degradation of ecosystem services as highlighted by the Millennium Ecosystem Assessment [392]. Given the importance of ES for human-wellbeing, their socio-economic values and whole-system relevance, ES provides a useful framework to examine biorenewable systems (e.g. bioenergy [396]) and the associated environmental, social and economic implications of deployment strategies. A range of ES evaluation frameworks have been proposed with no widely accepted approach [397] but they could be broadly classified as quantitative and semi-quantitative/qualitative approaches e.g. the matrix semi-quantitative approach proposed by Holland et al [398], quantitative approaches with indices of bird population trends for bioenergy and biofuel evaluation [399, 400]. The ES research on biorenewable systems have focused on the biodiversity and climate regulation induced by bioenergy and biofuels with other ES categories and bio-sectors less addressed. In general, the ES footprints change are not only driven by the biorenewable technology penetration but also vary with the spatial distribution and development status of natural capital resources (e.g. initial land cover), regional climate and time horizon[397]. As concluded by Fargione et al. [401], land use conversion from natural vegetation (e.g. rainforests) to 1G food-crop could generate bio-sector carbon debt in contrast to sustained GHG mitigation benefits offered by the waste-based bioeconomic systems developed on abandoned or degraded lands. In general, more positive effects of perennial 2G biomass on species and habitat diversity, and climate regulation have been observed [402-405] though the biodiversity implications could vary with the micro-management strategies in the fields [406]. A comprehensive review carried out by Immerzeel et al. [397] highlighted the drivers and trends of biodiversity as a consequence of bioenergy crop production, where land use change was identified as the most important driving forces, producing direct and indirect effects on native habitat change. As demonstrated in Figure 14, different taxonomic groups (plants, invertebrates and vertebrates) have been proposed as biodiversity impact measures to indicate the species composition, richness, evenness and abundance in response to the ecosystem change (e.g. land use change) [407, 408], where birds and beetles are the most studied taxonomic group [397, 409-413] with plant species biodiversity under-addressed. However, a recent global analysis shows that the ongoing extinction of plant species has been a missing biodiversity hotspot and deserves more efforts to achieve effective conservation planning [414].

In addition to biodiversity and climate regulation, other water, soil–based regulating ES as well as supporting, cultural ES have been investigated such as water regulatory [415-417], carbon and nutrient cycling [416, 418, 419], pollination [411] and recreation [420, 421]. Some regional or national level ES evaluation tools have been developed e.g. the EU BioScore ES model (Biodiversity impact assessment using species sensitivity Scores) developed for policy impact assessment [422], the UK national ecosystem assessment [423] and Intergovernmental Platform on Biodiversity and Ecosystem Services (IPBES – http://www.ipbes.net). Such ES evaluation frameworks offer powerful tools, which are ready to be linked with other modelling platforms to map out the ecosystem services change in response to biorenewable sector development.

In previous research, ES trade-off has been included in landscape decision [424]. Several mitigation strategies for realising a green economy while delivering multiple ecosystem services were concluded from previous research, which demonstrated the mitigation potential of both supply and demand sides. Supply-side strategies include multi-functional landscape planning [415], screening of resource-efficient and low-carbon biomass and technology, logistics and network design on degraded lands, closed-loop systems (e.g. pyrolysis biochar for enhancement of soil carbon sequestration); whereas the demand-side mitigation could be achieved via closed-loop economy (e.g. waste reduction) and shift in human behaviour and societal perception [409, 425, 426]. These supply-demand mitigation strategies offer promising strategic planning options, which could be explored in depth via softlinking ES evaluation tools with system optimisation approaches.

3.2.2 Life cycle sustainability assessment (LCSA)

LCSA refers to the evaluation of all environmental, social and economic impacts in decision-making processes towards more sustainable products throughout their life cycles [427]. Initiated from LCA, the life cycle thinking approach has been extended since 2002 to form a LCSA methodology framework, which consists of three pillars (Figure 14) - environmental life cycle assessment (LCA), life cycle costing (LCC) and social-LCA (SLCA) [427]. As a systematic and rigorous evaluation framework, LCSA provides integrative and holistic perspectives for multi-criteria decision on a given product system. As generalised in Eq. (1), LCSA accounts for all input-output flows occurring at each life cycle stage throughout the ‘cradle-to-grave’. Formalised by the International Organization for Standardization [428], E-LCA quantifies the environmental footprints associated with all stages of a product, service or process. LCC and SLCA examine the holistic economic aspects and social consequences respectively, evaluating the improvement opportunities of various product systems and processes including biorenewables.

$$EI_{kpi} = \sum_r \sum_s EIf_{r,kpi}^{in} X_{r,s}^{in} + \sum_c \sum_s EIf_{c,kpi}^{out} X_{c,s}^{out} \qquad (1)$$

Where the variable EI_{kpi} denotes the total sustainability impacts of a given process (per functional unit) expressed as key performance indicator kpi (e.g. global warming potential and cost). EI_{kpi} is determined by the characterisation impact factors for input resource r ($EIf_{r,kpi}^{in}$) or emitted compound c ($EIf_{c,kpi}^{out}$) and the input or output flows ($X_{r,s}^{in}\ or\ X_{c,s}^{out}$) at life cycle stage s.

3.2.2.1 LCSA methodology and overview

Under the guiding principles (life cycle perspective, transparency and completeness) [428], LCSA consists of four interactive phases (goal and scope definition, inventory analyses, impact assessment and interpretation) [427], capturing every life stage from raw material acquisition to final disposal. The first LCSA phase scopes the fundamental modelling elements including the system boundaries and the functional unit, and defines the principles and methodologies to be applied. At the inventory stage, data are collected on a unit process basis within the system boundary and assessed against data-quality requirements. Inventories are associated with the impact categories at the assessment stage, which comprises the mandatory element of characterization and possibly other optional ones (normalization, weighting). Inventory outputs are converted to category indictors using defined characterization factors, which can be further linked to category endpoints defined as 'attribute or aspect of natural environment, human health or resources identifying an environmental issue' in the case of E-LCA [429]; the aggregated indicator results provide characterized profiles of the studied products, which can be normalized to give information on relative magnitude of each indicator result. Life cycle impact assessment (LCIA) outcomes are presented in the interpretation phase in accordance with the study goal and scope to reach conclusions and recommendations. Generally, two types of LCA have been distinguished: attributional LCA (ALCA) and consequential LCA (CLCA) approaches. The former is a descriptive hybrid approach, based on process and input-output, focusing on the environmentally relevant flows to and from a life cycle and its subsystems; the latter is change-oriented, aiming to understand how environmentally relevant flows change in response to possible decisions [430]. Such emerging concepts could be further extended to LCSA, to represent the retrospective (attributional) and prospective (consequential) sustainability aspects. Although SLCA and CLCA have gained increasing attention in last decade, research on the LCSA methodology and applications still remain as a challenge due to the trans-disciplinary nature of LCSA and lack of robustly applicable methods for certain impact categories [431, 432]. A thorough literature review suggests that very few published research articles focuses on the holistic LCSA of biorenewable systems [432-439] but environmental aspects have been widely investigated. Amongst the large number of published LCAs on biorenewables, gasification (syngas for biomethanol or electrification), pyrolysis (biocrude oil), anaerobic digestion (biogas for electricity) and fermentation (bioethanol as transport fuels) have been the main research focus (see summary in Figure 13). High-value bioproducts via biochemical routes (e.g. biohydrogen, biobutanol, succinic acid, single cell protein, see Figure 12 and Figure 13) and the biorenewables derived from microbial clusters (e.g. microalgae) remain a critical research gap due to the lack of comprehensive data [440].

3.2.2.2 Biorenewable systems scope

LCSA is a relative approach with all the inputs-outputs and the environmental profiles generated being related to the functional unit; thus the functional unit forms the basis for LCSA evaluation particularly the comparison between counterparts. In biorenewable system, the functional unit could be defined as one-dimension (e.g. per energy or mass unit) or specified to reflect multi-dimensions (e.g. spatial and temporal, or other boundary dimensions). The former is a generally adopted approach in previous LCAs or LCSAs [439, 441]. Such one-dimensional physical measure-based unit generally reflects well the linear fossil economy nature. However it is not applicable to the multiple bio-product systems particularly those under circular bioeconomy, which concerns the natural capital resource flows, evolving multidimensional functions and closed-loop complexity.

The attributional static approach has been widely adopted in previous LCSAs on biorenewables. Few published studies expanded system boundaries accounting for implications of marginal variations (e.g. small-scale change of economic sector in response to demand change) [442-446] and effects of large-scale non-marginal variations (i.e. multi-market considering global equilibrium of all economic sectors) [447-450]. The latter expands consequential boundary further to account for the interactions and competition of multi-markets, multi-regions and capture wider socio-economic mechanisms; thus it represents an integrative tool placing regional decision-makers under a wider context and addressing the critical biorenewable-food competition issues effectively. This can be achieved by combining economic equilibrium model with CLCA [450, 451]. Further exploratory research focused on consequential LCSA robustness and representativeness of operational equilibrium model (technology choices); Kätelhön et al. [452] introduced a stochastic optimisation model in a CLCA approach, which captures multi-market dynamics meanwhile calibrating the result robustness.

Analysing attributional LCSA, the system boundary defined in studies can be broadly categorised as cradle-to-grave, cradle-to-gate (e.g. well-to-tank) and cradle-to-use (e.g. well-to-wheel). Most of the LCAs on bioenergy and biofuels scoped the system boundaries as cradle-to-use whereas the studies on biomaterial and biochemicals reflect their cradle-to-grave life cycles. These modelling choices matter, as the modelling approach often plays an important role in determining the environmental impact of a product [453]. However, as pointed out by Muench et al.[454], bioenergy systems involve three paths (biomass, conversion, distribution), thus a one-dimensional boundary definition overlooking certain path (e.g. electricity transition) is considered as insufficient for bioenergy evaluation. Similarly, a range of other biorenewables also involve multiple dimensions and even closed-loop issues e.g. waste-based biorenewable systems. As analysed in the previous section, carbon cycles underpin the biorenewable development. Therefore, a multi-dimensional boundary considering temporal and spatial scales and reflect the biorenewable system complexity and carbon circular nature from both attributional and consequential perspectives should be further explored.

3.2.2.3 Biorenewable carbon cycles and allocation approach

A range of carbon sinks and emitters are involved in biorenewable carbon cycles (presented in Figure 15), which can be summarised as below-

- The biorenewable resource production stage acts as a carbon sink sequestering biogenic carbon from the atmosphere into biomass and subsequent biorenewable products and accumulating soil carbon due to plant leaf litter and/or fine root biodegradation in soil.
- Carbon capture and storage (CCS) or utilisation processes involved in a biorefinery could potentially lead to biogenic carbon input flows e.g. the CCS capturing CO_2 emitted from fermentation of lignocellulosic feedstock.
- Biological or mechanical waste treatment options including anaerobic digestion or recycling for biopolymer disposal can also generate carbon sink effects by recovering biogenic carbon as biogas or petrochemical material substitution.
- The carbon sink effects of landfill depend on the temporal boundary (mid-term vs. infinite). Carbon emissions evolved at the resource production stage are mainly attributable to the agricultural field operations (fuel combustion and agricultural machinery inputs), agrochemical inputs and carbon released agricultural lands due to microbial soil respiration.
- Other carbon emitters including biorefining processes and disposal treatment also cause carbon release due to either chemical/biochemical/thermochemical reactions or operational inputs (including energy, chemical, and infrastructure inputs).

Handling such complex circular carbon systems remains as one of the controversial issues in LCAs [455] and can be a sensitive factor for LCSA allocation. For multiple-product systems, three allocation approaches are applicable to partition the material/energy flows and their associated sustainability impacts between the co-products i.e. allocation by physical relation (e.g. mass, volume etc.), allocation by economic values or system boundary expansion [456, 457]. In consequential studies, allocation by mass or economic values can be avoided by applying system boundary expansion [430, 458]. Although there is no universal consensus on the allocation methods in attributional LCSA/LCAs, the avoidance of allocation through system expansion (followed by physical-based allocation) has been indicated as the preferred approach for LCA in ISO LCA guidelines [457, 459] and PAS 2050 [460]. Literature reviews show that carbon neutral assumptions have been generally adopted for biomass and biorenewable system studies [454, 461-464]. However, assuming climate neutrality does not reflect the details of the biorenewable carbon cycles. Research efforts have been made to develop methods to assess biomass CO_2 climate impacts [465]. A stoichiometric carbon counting approach has been suggested to determine the effects of carbon sinks and emitters along the biorenewable upstream and downstream systems [365, 466]. Figure 16 shows the carbon removal potential associated with different sources of biomass.

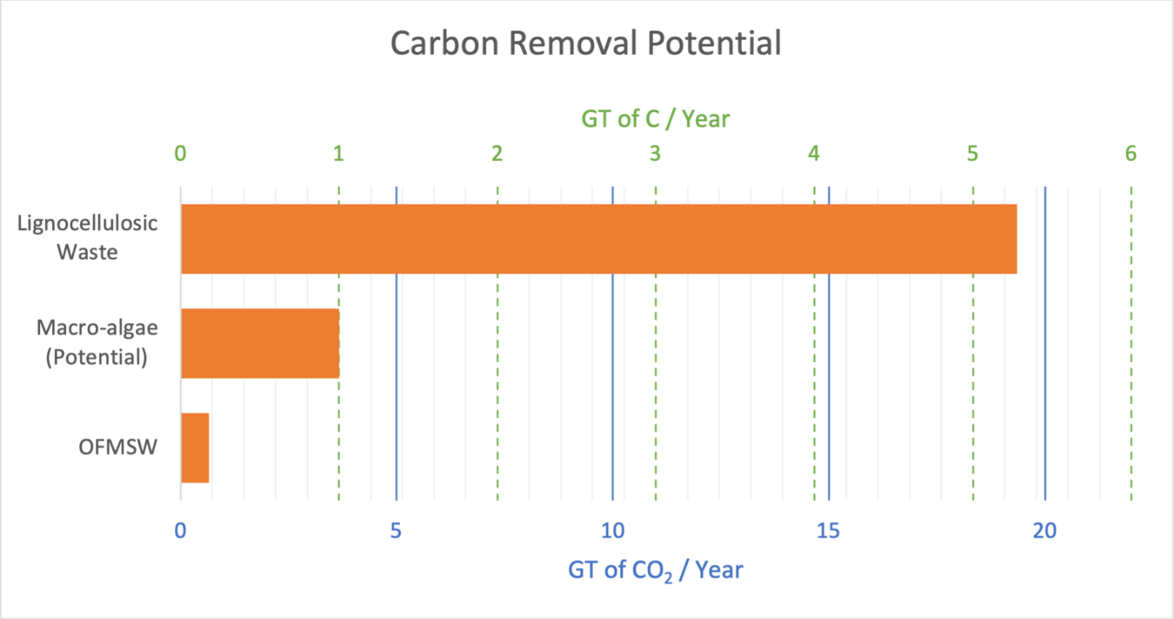


Figure 17: Carbon removal potential associated with different sources of biomass.
For reference, global anthropogenic CO_2 emissions, excluding land-use changes, were 36.1 GT in 2022 [467]. Figures refer to total available mass of carbon; many carbon removal technologies, such as biochar, have significant carbon losses [468]. Note some lignocellulosic waste is already used in ways that lead to some of the carbon being stored, such as biochar for soil improvement. Data from [469 (Supplementary Information), 470]. Calculations detailed in Supplementary Information SI-8.

3.2.2.4 LCSA criteria and impact assessment

In LCSA, the impact assessment methodologies can be categorised as midpoint (‘problem-oriented’) and endpoint-oriented (‘damage approach’) approaches [471]. The former is chosen along with environmental/economic/social mechanisms between the inventory results and damage-oriented endpoints [429] and the latter is defined at the level of protection areas [430]. These two approaches are differentiated by the way in which the sustainable relevance of category indicators is taken into account [472]. Unlike the midpoint approach with multiple environmental indicator results, at the end-point level the sustainable relevance of category indicators provides normalised single scores for decision-makers. But end-point results may be misinterpreted by overlooking the fact that single scores are subjective to the normalisation reference systems. Such a methodological choice can be a sensitivity parameter, which could be examined via data quality analysis [473].

In the previous LCSAs of biorenewables, global warming potential, energy efficiency, eutrophication and acidification, water and land use are widely investigated environmental indicators with other impact categories often overlooked [169, 173, 454, 474-480]. The key socio-economic indicators concerned in the published studies include the costs for CO_2 mitigation, capital inputs and operations, and the overall profit analyses [454], food and energy security, social-wellbeing (e.g. energy/facility accessibility, employment, poverty, work environment), social equality (e.g. human rights, corruption, education accessibility, community engagement) [481-487]. In comparison to LCA and LCC where quantitative characterisation models (e.g. CML, TRACI, Eco-Indicator, Recipe) are available and widely applicable, SLCA studies mostly were based on interviews and observations [488] without consensus on the impact assessment methodology. As pointed out by Robledo-Abad [485], the advancement of LCSA knowledge vary with regions with better understanding on economic and environmental categories in developed regions in contrast to the emerging economy, where more LCSA attention has been paid to socio-economic aspects. To determine whether biorenewables deliver progress in achieving sustainability goals, holistic and reproducible LCSA are needed to avoid inadvertent ‘problem shifting’ thus further research efforts are required on SLCA methodology development.

Climate, temporal and spatial variability in LCSA have been recognised as a research gap and as being critical for economic and environmental planning, regional evaluation of technology viability for biorenewables especially from spatially distributed resources (e.g. agriculture residue) [475, 489, 490]. Particularly, spatial LCA models with region-representative data and characterisation indicators have been highlighted in UNEP-SETAC guidelines as a conceptual framework for LCA and ES. This is especially the case for the assessments for land use decision-support at global or regional scales with spatial diversity [491]. However, in comparison with the large number of LCSA studies adopting country/region/industrial average data inventory (e.g. NREL US LCI databases [492], Plastics Europe [493]) , limited spatial or dynamic LCSA studies have been published on biorenewable systems so far with focus on the biodiversity, energy and GHG footprints in response to land use change or distributed resource use [474, 478, 479, 494]. Humpenoder et al. [495] published a GIS based LandSHIFT model soft-linked with LCA to estimate spatially-explicit GHGs of LUC due to 1G biofuels in the EU considering the soil and climate variation. Gasol et al [496] studied the cradle-to-gate GHGs of electrical and thermal power derived from hardwood (poplar) at spatial scales accounting for climate variability. Roostaei and Zhang[497] proposed a HRSE-LCA framework integrating Geographic Information System (GIS)-based resource assessment and algal growth model with LCA to analyse the production potential, energy and GHG profiles of pyrolysis and HTL bio-fuels processed from wastewater-cultivated algae at USA national scale. In addition to the region-representative data, the regionalisation of characterization models and indicators are desirable for science-evidenced decision-making. Spatially-explicit LCA characterisation factors and indicators in water and land use, acidification and eutrophication have been studied [498-501] but are not yet included in the assessment literature [502]. Uncertainties at the methodological level remain a research challenge [503]. Overall, GIS-based LCSA approaches can be an effective tool for spatial-temporal sustainability assessment but need great research efforts at both the methodology and data levels.

Regardless of spatial variability, economic and technological impacts were more generally regarded as positive in previous research whereas the negative scores on most social and environmental aspects (except for GHG accounting for fossil substitution effects) were often reported for bioenergy and other value-added biorenewable systems [485]. For terrestrial resource-based biorenewables, the agriculture cultivation and biorefinery processing stages have been identified as hotspots, contributing significantly to the overall impacts [439]. For aquatic biomass or waste based biorenewables, conversion technologies dominate the overall impacts with the cultivation stage potentially bringing environmental savings (e.g. nutrient recovery and CO_2 sequestration) [173]. Due to such environmental savings, 3G biofuels have been indicated as superior systems over 1G and 2G on GHG balance and land use but 1G and 2G biofuels were evidenced as more efficient in terms of energy utilisation (energy ratio and energy return on investment as indicators) based on the previous research observations [504]. Moreover, the uncertainties in 3G biofuel scaling-up and its economic viability hinder the commercial progress [504]. Such trends could also represent the general comparison between 3G biorenewables and 1G/2G counterparts, with the exception of the high-value compounds potentially extracted from 3G resources (e.g. pigments, polyunsaturated fatty acids, anti-oxidants), which are still not well understood in terms of their sustainability performances [504]. The comparison between centralised and decentralised systems vary with the regional feedstock characteristics and synergies amongst technologies [505, 506]. Studies carried out on lignocellulosic biofuel production systems concluded that decoupling the pretreatment from fermentation to densify the biomass locally via decentralised processing depots reduces the collection radius for bulky biomass and creates a local closed-loop system [505]. Thus depots could deliver better GHG and energy profiles than the centralised processing systems [490, 505, 507] but represent more economically viable solutions for perennial crops than for annual crops [490, 508]. Different conclusions were reached from waste recovery studies. Driven by conversion efficiency, centralised CHP systems outperformed the decentralised combustion technology in terms of sustainability for processing sugarcane residues or biogas [509, 510]; whereas decentralised anaerobic digestion (AD) system were reported as a more environmentally favourable choice than centralised system for OFMSW and sludge treatment [511]. The LCSA hotspot (also called contributional) analyses and comparison not only can inform decision-makers to set performance targets and identify improvement opportunities but also provide ‘plug-and-play’ input-output modules for system-level decision-making tool underpinned by life-cycle thinking.

3.2.2.5 LCA and planetary boundary

The planetary boundaries (PB) framework defines a safe operating space for humanity based on the biophysical processes that regulate the stability of the earth system [512]. Specifically, planetary boundaries were proposed for nine earth system processes - climate change, change in biosphere integrity (biodiversity), stratospheric ozone depletion, ocean acidification, biogeochemical P and N flows, land systems change, freshwater use, aerosol loading and introduction of novel entities (chemical pollution) [8, 9]. While many studies focus on carbon footprint as a measure of environmental impact, Tulus et al. [513] found that for many chemical goods, carbon footprint correlates poorly with sustainability as assessed by the planetary boundary framework. Recent efforts have been placed on the methodology development to integrate LCA into the PB framework. These include the exploratory research to link LCIA characterisation models and impact categories with PB control variables [514], and the introduction of the concept of absolute sustainability, an approach to LCA that aims to incorporate the planet’s carrying capacity into LCA-based PBs indicators [515, 516]. The PB framework has been applied in previous research to address future sustainable food supply within four boundaries i.e. climate change, land-system change, freshwater use and biogeochemical N/P flows[517, 518]. Notably, despite two-level hierarchy of boundaries has been proposed [8, 9] , where climate change and biosphere integrity are recognised as core PB, the proposed boundaries are interdependent. In addition, the PB framework recognises an integrative approach coupling boundaries and highlights the importance of dynamics at Earth subsystem level on the functioning of whole Earth system. Although PB framework is not designed to be downscaled [9], LCA research community explored the methods to disaggregate PB to sectoral and national levels by introducing allocation approach based on global demographic trends; further life cycle inventories was linked with planetary boundaries to investigate sustainable design of national energy systems [519]. Research was also published to integrate process design and LCA to quantify the contribution of biopolymer production [520] to mitigate climate change within PB boundary.

Since the LCA approach formalised in 1990s, numerous efforts have been placed to develop quantitative methods to characterise the environmental impacts and to build database representing the industrial/sectoral technologies and processes. Undoubtedly, LCA database and methodological advances offer powerful tools to support decision-making on sustainable development and design of biorenewables [521]. However, LCA framework only enables data analyse and evaluation functions but does not inform design problems within an Earth-system safe operating space, which consists of interactive environmental boundaries across regional and global scales. Methodology underpinned by LCA and PB framework offers a quantitative approach to develop fundamental understanding of the sustainability implications of biorenewable systems on the functioning of the Earth system. This represents a future research direction.

3.2.2.6 Deterministic vs. stochastic LCSA and dynamic LCSA

The majority of the LCSA studies reviewed above can be defined as deterministic LCSA, which does not take into account the data quality, stochastic and dynamic aspects of the systems under investigation. In contrast, the LCSA developed in a statistical framework can be classified as stochastic LCA [522].

LCA data quality analyses include sensitivity and uncertainty analyses. Sensitivity analysis has been carried out in previous research to test system boundaries [473, 523], temporal effects [524-526], allocation approach [527, 528], parameter values [529-531] and characterisation methods [473, 532]. Different sensitivity analyses techniques were proposed, amongst which scenario analysis is a widely applied method [533]. The method involves calculating different scenarios, to analyse the influence of input parameters on either impact assessment indicator results or ranking; two types of possible analyses can be distinguished 1) contribution to variance to determine the implications of uncertain parameters to the output variance; 2) screening to identify the significant parameters [534].

Another data quality analysis component - uncertainty analysis - is not commonly performed in the LCSA of biorenewables, [535] although research efforts have been made on the classification, definition, and sources of uncertainties as well as methodological aspects for expressing uncertainty [522, 525]. At the inventory level, the uncertainties are introduced into LCSA systems due to the cumulative effects of input uncertainty and inventory uncertainty sourced from data gaps, which can be evaluated via data quality indicators (temporal, geographical, or technological coverage, data reliability or completeness). A methodology framework combining statistical methods and pedigree matrix has been proposed to quantify the uncertainty in inventory and LCIA indicator results [525]. Under the framework, maximum likelihood estimation and goodness of fit were proposed for analysing the operational data with multiple measurements or simulated computational inventory containing variability parameters. Pedigree matrix originally developed Weidema and Wesnæs [536] and widely applied to the LCA database e.g. Eco-invent has been adopted to transform the data quality indicators to probability distributions ('default' lognormal distribution); whereas probabilistic Monte Carlo simulation was suggested to estimate the uncertainties of LCSA outcomes resulted from the statistical variability or temporal, geographical or technological gaps in the inventory [532]. Monte Carlo simulation combined with fuzzy datasets and pedigree matrix have been well demonstrated to quantify the uncertainties of biorenewable systems e.g. 2G and 3G biofuel [535, 537-539]. To overcome the limitation of Monte Carlo approach, that is the high computational time required due to searching the uncertainty space for all stochastic variables, other methods such as reliability approaches [522, 540], Latin Hypercube Sampling, and quasi Monte Carlo [541] have been proposed in stochastic LCA studies to approximate the LCSA decision confidence. A similar approach uses Sobol indices to identify the most sensitive parameters, which can then be used to simplify the uncertainty estimation [542]. However, such approaches have not been yet applied to biorenewable studies. As highlighted in previous research [543], sensitivity analyses combined with uncertainty analyses can lead to an increase in confidence in the findings which suggest that LCSAs lacking explicit interpretation of the degree of uncertainty and/or sensitivities should not be used as robust evidence for decision or comparative assertions. Thereby, it is recommended to incorporate data quality evaluation into the future LCSAs of biorenewables and bridge the knowledge gaps.

Either deterministic or stochastic LCSAs reviewed above mainly focus on developed or steady-state products or systems; for emerging and evolving systems with complex and dynamic nature and great uncertainties due to incomplete inventory, several different modelling approaches including scenario-based, trend analysis and agent-based models (ABM) have been proposed for dynamic LCSA. Miller et al [544] presented a dynamic framework coupling ABM and ALCA, where the probabilistic behaviour of decision-makers e.g. technology developers were captured using a Bayesian statistical approach and a range of what if scenarios were investigated. Further exploration focused on the convergence of LCA with a complex economic model and agent-based simulation to capture the dynamic system driven by human behaviours [435]. Baustert and Benetto [534] reviewed the ABM and CLCA coupled models and addressed the uncertainty sources and system variability issues as well as methodologies in stochastic modelling. In addition, a Wright's law learning curve reflecting the relationship between technology costs and cumulative production has been incorporated into the dynamic LCSA framework to capture the 'learning-by-doing' effects on technology operation, economic and environmental performances and entire supply chains [545-548]. However, only very few biorenewables studies have adopted such dynamic LCSA approaches [547, 549], which remain a critical research challenge.

3.3 Data model in geographic information systems

The use of geographic information system is recognized as an efficient approach to analyse complex spatial phenomena and has been used to model various applications at multi-levels spanning from biomass resources (e.g. waste resources potential) to conversion technologies (e.g. waste treatment). Despite of the capability of spatial data acquisition, storage, processing and analysis, GIS alone does not allow for incorporating the decision maker's preferences and heuristics into the problem-solving process. Thus a range of GIS-aided methodologies e.g. multi-criteria decision analysis, fuzzy multi-criteria decision making and mixed integer programming models have been developed and applied to spatial decision support in the waste sectors [550-552] (particularly in MSW collection and monitoring[553]), as well as the spatially-explicit evaluation, monitoring and planning of terrestrial and aquatic biomass [497, 503, 554, 555]. Since the 1990s, when a spatial LCA tool was proposed by Bengtsson et al. [556], GIS coupled with LCA has been used to represent the specially-explicit LCA sub-system layers (technical, environmental and social) and applied to sustainable planning and analyses of biosectors, particularly those associated with uneven resource distribution (e.g. agro-residue derived bioenergy [503]) or bounded by the geographically differentiated factors (e.g. infrastructure [557], climate[558]). The development of a leading platform Open-LCA reflects the GIS-aided LCA research advances in recent years. Open-LCA is an open-source Java application running on Eclipse Rich Client Platform. It enables LCA collaborative server and embeds GIS-aided LCA models. OpenLCA is the first and only LCA platform to enable database/model development in a distributed and paralleled collaboration manner across users, servers/repositories. In comparison with other widely adapted LCA software (e.g. Simapro and GaBi), very few studies have explored GIS-aided LCA using Open-LCA platform [559].

Besides, GIS-aided LCA models have been presented for linear or non-linear ecosystem services assessment, especially provisioning, regulating ES impacts (e.g. biodiversity, erosion regulation) in response to the change in the natural capital resource patterns (e.g. water, land) [407, 560-562]. Considering the biorenewable system features (e.g. uneven distribution, linked with geographically varied ecological drivers), GIS coupled with remote sensing undoubtedly offers an effective way to acquire, process and analyse spatial data. One of the promising research directions lies in the GIS-aided model integration, covering the multi-geographical level decision-making (farm level combined with regional network) and linking the spatially-explicit ecosystems with biorenewable technosphere.

3.4. Process simulation and techno-economic evaluation

As highlighted in Figure 11 and Figure 12, process design and simulation studies are dominated by thermochemical routes (torrefaction, pyrolysis, gasification and hydrothermal liquefaction), fermentation (bioethanol, succinic acid, lactic acid) and anaerobic digestion. A significant modelling gap has been identified in high-value biorenewable conversion processes (especially new food/feed sourced from microbial fermentation). Via a review of state-of-the-art modelling approaches, the sections discuss the research opportunities in process simulation.

3.4.1. Kinetics vs. thermodynamic equilibrium models

Models for simulating biorenewable conversion technologies can be largely divided into two groups: kinetic and thermodynamic equilibrium models. The former is used to predict the progress and the product compositions along the reactions; whereas the latter also denoted as zero dimensional, can be used to project the theoretical efficiency and achievable yields of desired end-reaction products based on the assumption that reacting systems reach steady state with minimised Gibbs Free Energy (maximised entropy) [563-565]. Despite the simplified formulation and wide applicability, the latter is not capable of describing the instantaneous product distribution along with the geometric dimension, thus cannot be used for reactor analysis or design [563, 564]. Equilibrium modelling consists of two approaches– 1) stoichiometric models which require well-defined reaction mechanisms, chemical reactions and species involved; 2) non-stoichiometric models, which are effective to identify the chemical compositions when the reaction paths are not yet known [566]. Both kinetic and equilibrium models have been embedded in commercial process simulators such as AspenTech modules (Aspen Plus or Hysys), where the physical relationships, thermodynamic equilibrium and rate equations have been built in to enable the process flowsheeting, plant-wide process behaviour projection.

3.4.2. Process simulation

Process simulation is a model-based representation of chemical, physical, biological, and other technical processes and unit operations in software. It is used for the design, development, analysis, and optimisation of biorenewable processes such as biomass plants, biomass thermochemical conversion processes, power station and biomass biological conversion processes.

The advantages of process simulation are to (a) reduce plant design time by allowing designers to quickly test various plant configurations (b) improve current processes by answering ‘what if’ questions, determining optimal process conditions within given constraints and assisting in locating the constraining parts of a process. The ultimate objectives of using process simulation are to realise faster troubleshooting, online performance monitoring and real-time optimisation.

A variety of modelling platforms e.g. Aspen Plus, Aspen Hysys, SuperPro Designer, Modelica, GPS-X (for Anaerobic digestion) provide a resource where researchers and engineers can model, simulate, design, optimise their processes; conversely, the outcomes (e.g. technical reports and publications) can enrich the platforms about biorenewable systems by sharing information of specific case studies, identifying the model limitations, and extending the model applicability.

The first challenge for researchers using modelling platforms is to identify the available physical and chemical properties in the database which include pure component and phase equilibrium data for conventional chemicals, solids and polymers. Subsequently, the additional data about thermodynamics and dynamics need to be added by researchers as biomass feedstocks and their intermediate and end products have a complex composition with sophisticated reaction path. For example, tar formation in biomass pyrolysis and gasification is complex. Mellin et al. [567] presented a comprehensive chemistry scheme (134 species and 4169 reactions) to describe tar formation using CHEMKIN. El Wajeh et al. [568] developed a mechanistic model with rigorous thermodynamics for biodiesel production.

The second challenge for researchers using modelling platforms is to integrate solids, batch and custom processing unit modelling. For example, fluidised beds of biomass gasification are used as a technical process, which has the ability to promote high levels of contact between gases and solids (e.g. biomass, sand and catalyst). However, there is a lack of a library model to simulate fluidized bed unit operation in widely used commercial platform (e.g. ASPEN PLUS). It is possible for users to input their own models, using FORTRAN codes nested within the ASPEN PLUS input file, to simulate operation of a fluidized bed[569].

3.4.3. Computational Fluid Dynamics (CFD) for unit operation

CFD is a powerful tool which uses numerical analysis and data structures to model and analyse biomass conversion processes that involve complex multiphase fluid flows with mass, momentum and heat transfers. To simulate unit operation, CFD is the most-powerful numerical tool available, empowering researchers to achieve economic and environmental targets as they optimise reactor and product's performances. Widely used commercial software of CFD includes well-validated physical modelling capabilities to deliver fast, accurate results across the widest range of CFD and multiphysics applications. CFD modelling has been successfully implemented on various biorenewable systems e.g. pyrolysis [570, 571],gasification [572, 573], combustion [574, 575], liquefaction [576], anaerobic digestion [577, 578], fermentation [579]. CFD can be used to model reactors across a wide array of physical scales, from milli-scale to full industrial scale [577, 580].

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capabilities to deliver fast, accurate results across the widest range of CFD and multiphysics applications. CFD modelling has been successfully implemented on various biorenewable systems e.g. pyrolysis [581] [582],gasification [583] [584], combustion [585] [586], liquefaction [587], anaerobic digestion [588] [589], fermentation [590].

The advantages of CFD modelling are to (a) reduce time and costs for new design of reactor; (b) analyse biorenewable problems when experiments are relatively difficult and dangerous (e.g. high temperature and pressure); (c) offer the capacity of studying biorenewable systems under extreme conditions over practical limitations. The disadvantages of CFD modelling are: (a) it is usually necessary to simplify mathematically the phenomenon (e.g. chemistry or turbulence) to facilitate calculus; thus the result accuracy depends on mathematical simplification; (b) there are several incomplete models to describe the turbulence, and multiphase phenomena; (c) untrained users of CFD have the tendency to believe that the output of the computer modelling is always accurate.

CFD model for liquid and gas phase in biorenewable problems are relatively robust. The promising future directions of CFD modelling on biorenewable problems are - to improve modelling accuracy of multiphase phenomenon, particularly for particle flows. There are two main methodologies, Eulerian and Lagrangian, to model particle flows in biorenewable problems. The Eulerian model of particle flow is a way of looking at particle motion that focuses on specific locations in the space, through which the particle flows as time passes. The Lagrangian model of particle flow is to investigate particle motion, where the observer follows an individual particle parcel as it moves through space and time. Xiong et al. [591] pointed out the improvement of particle flow modelling. The Eulerian method requires in-depth development on the effects of sub-grid structures such as particle clustering, size distribution, and temporal changes of particle size and shape. The Lagrangian method necessitates accurate but computationally efficient sub-models to consider the influence of intraparticle transport phenomena. Additionally, the high computational cost of CFD modelling is another conundrum when simulating large industrial scale systems, especially when the Lagrangian method is applied. Recently, advancements in supercomputing and parallel computing, and their wide connections to the field of research and development, mean that digital twins of large-scale unit operations using a CFD framework are becoming a more realistic prospect.

3.4.4. Multi-scale process simulation

Often, it is challenging to determine the correct scale to capture a phenomenon of interest as multiple phenomena interact at different scales. Multiscale modelling attempts to address this problem. Its importance as a tool in sustainable development was noted by Pistikopoulos et al. [592]. Multiscale process simulation and design of biorenewable systems are becoming more attractive, and the main challenge is to determine the models to run and how they iterate/interact. The fast and robust coupling approaches (manual or automated) are essential to advance the development of multiscale process simulation.

Abdelouahed et al. [593] proposed an approach to couple Aspen Plus and Fortan modules to include detailed chemical mechanisms in process simulators without thermodynamic equilibrium assumptions. Using CFD in conjunction with Aspen Plus has been suggested as an alternative approach i.e. CFD-generated residence time distribution curves were formulated as compartment model under Aspen Plus environment to derive process flowsheet configuration and mass/energy balances [565, 594].

3.5 Process synthesis and planning

Process-synthesis and planning is a broad area in process system engineering (PSE), covering a wide range of design problems related to manufacturing from an enterprise-centric perspective. The key decision variables concerned in the biorenewable conversion systems can be summarised as follows:

- The decision on manufacturing process units and interconnection, unit operation configuration (e.g. temperature), input/output flows and composition;

- Strategic decisions e.g. investment in new facilities, plug-and-play solutions to existing facilities, closure of facilities, process repurposing or substituting;
- The location and logistics decisions, e.g. location of new facility, supply sourcing;
- Tactical planning on production, inventory and material flows;
- Operational decisions e.g. scheduling, batch vs. continuous processing.

This section will focus on two levels – single-site and multi-site optimisation.

3.5.1 Conversion process synthesis

At single-site biomass conversion level, PSE has been playing significant roles in advancing the computer-aided process and reaction network design. Process synthesis determines the flowsheet and equipment for given feed and product streams. It is a highly complex problem, with a search space that can be very large [595]. Commonly applied techniques for synthesizing process flowsheet include knowledge-based systems/artificial intelligence, thermodynamic methods (e.g. pinch analysis, energy analysis), meta-heuristics, hierarchical design and superstructure-based optimisation [596-598]. Knowledge-based systems have been applied to conventional waste treatment decision-support [599] but more exploration on artificial intelligence supported dynamic design has emerged as a new research direction. Other techniques including pinch analyses, energy analyses and hierarchical decomposition have been evidenced to be effective in process industrial applications [596] with the potential to contribute to sustainable bio-product synthesis [600-602]. These concepts were further combined with mathematical programming approaches to support process design. Under the mathematical programming framework, the representative superstructure-based synthesis problem is defined with given sets of feedstock and product streams and alternative processing units; a mathematical optimisation is further formulated to define the objective functions and a range of continuous and discrete variables. Such superstructure-based optimisation model often lead to mixed integer programming (MIP) problems, which can be generalised as follows -

$$
\begin{gathered}
Min\left(f_1(x,y)\ldots\ldots f_k(x,y)\right)\\
s.t.\, h(x,y)=0\\
g(x,y)\le 0\\
x\in\mathbb{R}^n\\
y\in\{0,1\}^m
\end{gathered}
$$

Where $f_1(x,y) \ldots f_k(x,y)$ denotes the objective functions consisting of conflicting multiple objectives. The continuous variables x are normally non-negative, presenting the input-output flows and compositions as well as certain design and operational decisions; discrete variables y define the selection of process units/locations etc. and their interconnections. Both continuous and discrete variables follow the equality constraints $h(x,y)$ e.g. material balance and inequality constraints $g(x,y)$ and satisfy the design specifications (e.g. production discharge allowance, physical operational limits and demands) and logical constraints.

In contrast to the conventional fossil-based processing industry, biorenewable conversion synthesis problems are characteristic of carbon flows from carbon sequestration via photosynthesis to carbon transformation to bioproducts. This has been captured in the published superstructure-based optimisation studies integrated with life cycle approach. Chen et al [603] presented a process synthesis optimisation problem for the poly-generation system using biomass and coal as feedstock for power, biofuel and chemical production. They explored the carbon taxation effects of the carbon capture and storage via biomass use. Wang et al [604] formulated a multi-objective mixed integer nonlinear programming (MINLP) model to investigate the trade-off between cost optimal and GHG minimised solutions for thermochemical conversion processes of lignocellulosic resources to hydrocarbons. In their study, the LCA end-point characterisation (Eco-indicator 99) method was introduced to set the upper boundary for threshold constraints on gate-to-gate overall environmental impacts, with the carbon accounted for by using a carbon counting approach. Later, this attributional life cycle optimisation framework was expanded to include consequential perspectives, where a deterministic MINLP model was formulated to optimise the production network for microalgae biofuel and both GWP mid-point and Recipe end-point characterisation models were applied [605]. They adopted a system expansion allocation principle to account for the changes in environmental impacts caused by the system decision with boundary expanded to include the upstream and downstream markets change as a consequence of algae biofuel production. This represents an emerging research direction where a systematic comparison between attributional and consequential life cycle optimisation deserves further research attention.

Martin and Grossmann [606] formulated a MINLP superstructure optimisation model to derive energy-optimised solutions for switchgrass-based bioethanol via gasification route where the optimisation problem was decomposed to eight sub-problems and pinch analyses was applied for heat integration. A decomposition principle was introduced to another methodology study to decompose the biorefinery synthesis optimisation model into sub-problems to solve the possible pathways while considering global optimal solutions [607]. The research group from Texas A & M University employed a branch-and-bound algorithm to solve a large-scale non-convex MINLP optimisation model and optimised a range of process synthesis problems on biofuel and bio-chemicals derived from MSW [608] wastewater and lignocellulosic biomass [609-611] via integrated thermochemical and biochemical routes. The studies reviewed above were based on deterministic optimisation frameworks with the processes formulated by adopting publically available results from either simulation (e.g. NREL studies) or laboratory work [612], and the life cycle inventory retrieved from available databases e.g. Ecoinvent [604]. Puchongkawarin et al [613, 614] presented an integrated superstructure-based modelling framework for wastewater recovery process synthesis by incorporating process simulation, life cycle approach and optimisation. These authors proposed an iterative approach to 1) feed the surrogate models constructed from state-of-the-art WWT simulators (GPS-X) and performance regression approximated from the techno-economic and LCA evaluation to the multi-objective MINLP optimisation model to generate the Pareto frontiers for the trade-offs between maximised net present value (NPV) and minimised GHG and eutrophication; 2) to refine and verify the process design by feeding back the optimal design solutions until model convergence.

In addition, mixed integer linear programming (MILP) models have been developed and applied for process synthesis particularly for metabolic pathways [615]. A reaction-network-flux analysis (RNFA) has been developed by a research group from RWTH University [616]. The MILP optimisation-based RNFA has been applied as a screening method for ranking and identifying optimal routes amongst a large number of alternative reaction pathways for a wide range of novel biofuels (e.g. furan, 2-methyfuran, butyllevulinate) generated from lignocellulosic biosynthesis [612]. The authors further extended RNFA to include sensitivity analyses to account for the parametric uncertainties in the reaction efficiency and achieved robust ranking [617]; their results highlighted promising alternatives to bioethanol (ethyllevulinate and 2-methyltetrahydrofuran) and concluded that lignin-based biofuel is considered as not competitive in terms of costs and environmental impacts (evaluated using end-point approach Eco-indicator 99). Kim et al [618] presented a superstructure-based MILP framework for biofuel conversion system configuration considering 1G and 2G biomass. In their study, the reaction network was explored from both bottom-up and top-down perspectives (i.e. optimal strategy for a desired product, optimal utilisation of a given feedstock). Bao et al [619] presented a MILP model to screen alternative reaction pathways and determine the biorefinery network configurations to meet a certain objective, where a case study is given considering thermal (gasification) and biochemical routes (AD and fermentation). In addition to reaction and process networks, MILP has also been introduced in the process configuration e.g. separation. Kong and Shah [620] presented a MILP optimisation approach for the conceptual design of an economic optimal reaction distillation system; this framework can be further expanded for the wider applications in biorefinery process design with multiple design criteria. The biorefinery process synthesis design problem is also one of three used by Martin et al.[595] to highlight the need for further development of computational design tools in process systems engineering in order to deliver on sustainable development objectives.

3.5.2 Enterprise-wide optimisation

At the multi-site level, wider temporal and spatial scales are involved; enterprise-wide optimisation (EWO) has emerged as an effective approach to solve the design problem. EWO involves optimising the operations of supply, manufacturing (batch or continuous) and distribution in an enterprise [621] with some overlap with the term ‘supply chain management’. In contrast to supply chain modelling, EWO focuses more on the manufacturing stages of a process industry with emphasis on their planning, scheduling and control. This often involves nonlinear programming (e.g. MINLP) due to the realistic manufacturing presentation (e.g. capacity) [596, 621], although Toorajipour et al. [622] noted an increase in academic research using AI-based methods . Compared with widely adopted supply chain optimisation, EWO applications in biorenewable system design are rather limited.

Sitting at the interface of PSE and operations research (OR), EWO has received increasing recent interest with many models developed for fossil-based process industry in both OR and PSE fields. Grossmann [621] reviewed the development and the challenges on multi-scale EWO, uncertainty and algorithms. The long-term strategy (e.g. investment) need to be coordinated with the medium-term tactical decisions (e.g. production, planning and material flows) and the short-term operational decisions (e.g. scheduling and control); uncertainties vary with different scales thus how to account for stochastic variations remains an unsolved issue. The author [621] pointed out the development of advanced computational algorithms and grid computing toolkit are needed for solving such large-scale EWO problems with uncertainties (e.g. demands, capital inputs). Later, Grossmann [623] presented a follow-up review of the mathematical programming techniques (e.g. MIP, stochastic programming and decomposition approach) applied to the EWO research and highlighted EWO features i.e. the integration of internet of things (IoT) data with decision-making across enterprise-centric multi-scale functions. The incorporation of economic and environmental sustainability criteria into multi-objective EWO was discussed by Grossmann and Guillén-Gosálbez [596] with an overview of the mathematical modelling techniques.

EWO applications so far range from petroleum industry [624] to pharmaceutical sectors [625]. Especially under the Industry 4.0 strategic initiative proposed in 2013 [261], multi-scale EWO is expected to play a more significant role. Industry 4.0 envisages factories and supply chains where products and machines are all connected to achieve inter-connective communication, and smart collection and analyses of data, as well as the co-ordinated processes in a distributed fashion [261]. This industrial revolution is expected to bring new business models, enhanced collaboration across the supply chain and information-track capability for identifying individual resource and products [626]. Data-driven EWO can deal well with multi-scale optimisation problems, with van de Berg et al. [627] showing that distributed data-driven EWO can in some cases recover the performance of the centralized problem formulation. Thus EWO and data-driven integrated approaches can be used to bridge the long-term design problems (e.g. process and network design) with medium and short-term objectives (such as responsiveness and flexibility at operational level).

Several optimisation methods have been proposed for solving multi-scale problems in manufacturing systems. For process scheduling at multi-site, the existing scheduling formulation can be broadly classified into discrete-time and continuous-time approaches. The most generally-adopted unified frameworks for process representations (State-Task and Resource-Task Network (RTN)) have been developed based on discrete-time scheduling formulations [628-630]; this has been further explored to reduce computational time by deploying different optimisation techniques (e.g. linear programming relaxation of MILP) [631]. Later, the unified framework was extended to RTN-based rolling horizon algorithms, which enable to solve large-scale optimisation problems and reduce computational time[632].

Due to the inherent limitations of the discrete-time approaches, significant research efforts were also devoted to develop continuous-time representations, [633]. To bridge multi-scale optimisation problem, Maravelias and Grossman [634] formulated a large-scale MILP model to optimise the short-term scheduling, process network design and capacity planning for batch manufacturing facilities, where the discrete uncertainties in raw material prices and final product demands were captured. The derived large-scale MILP model was solved using a Lagrangean decomposition heuristic algorithm [634]. Later the simultaneous short-term batch scheduling and middle-term planning for a single-unit continuous multi-product system was optimised using a MILP model [635]. To improve the computational tractability, the authors proposed a bi-level decomposition algorithm to solve this MILP for large-scale design problem in a continuous plants with multiple units operated in parallel [636]. More recently, two algorithms (bi-level and Lagrangean decomposition) were compared [637, 638]; the results demonstrated bi-level decomposition as a superior approach in terms of computation time for solving the multi-period MILP model to achieve the simultaneous multi-site solutions for capacity transformation via reactor modification(or batch scheduling) and production-distribution network planning.

The optimisation frameworks reviewed above could potentially be applied to design the highly customised batch operation system under Industry 4.0, where the users can adjust smart factory configuration through remote/control terminals and data advances [639]. In addition to the supply side, EWO is also proposed to explore industrial demand side management across multi temporal and spatial scales such as 1-year electricity demand scheduling integrated with long-term procurement problem [640]. Compared with the petroleum industry, little research has been carried out on the applications of EWO in biorenewable multi-scale optimisation. A MILP model was presented to solve the bioethanol-gasoline integrated system, which bridged several level design problems including short-term scheduling (e.g. sales at retail centre and batch production), medium-term planning at biomass cultivation and fuel production sites (e.g. capacity , resource flows) and long-term strategy (e.g. location and capacity planning) [641].

3.5.3 Research challenge

Overall, biorenewable production systems differ substantially from conventional petroleum chemical industry due to the carbon circular nature, underlying uncertainties and the digital transformation potential under Industry 4.0. There exist ‘smart and circular manufacturing system’ opportunities in biorenewable sectors where process synthesis and EWO are effective approaches for exploring enterprise-centric optimal configurations. The identified example systems and research opportunities include -

- Process synthesis for closed-loop systems with biorenewable production from waste resources to capture and fix atmospheric carbon dioxide and recover other pollutants;
- Biogenic carbon circular bio-refinery network design for phototrophic microbial carbon fixation and biorenewable synthesis;
- Operational decisions and tactical planning under digitalisation and industry 4.0 – batch processing with optimised responsiveness, flexibility and resource-use efficiency;
- Strategic decisions on process/infrastructure repurposing or substituting to achieve the transition from petroleum to biorenewable production system;
- Multi-scale biorenewable enterprise optimisation problems to bridge the strategic and tactical planning with operational decisions and incorporate the stochastic variations.

3.6 Supply chain optimisation

As discussed in the previous reviews [642, 643], supply chain (SC) optimisation concerns multi-site operational decisions on manufacturing and distribution, including upstream biomass cultivation, biomass and waste collection, pretreatment and conversion, downstream distribution and storage. Compared with the petroleum sector, biorenewable supply chains are complicated by their interconnection with ecosystems and built environments, and multi-echelon complexity with new agent groups and SC structure evolved from the bioeconomy transition. A number of excellent reviews have been published on supply chain optimisation [643-647]. Instead of a broad coverage of SC studies, this section reviews state-of-the-art model advances in multi-echelon and multi-scale biorenewable value chain design, analyses the biorenewable SC characteristics and proposes future research opportunities.

3.6.1 Overview of terrestrial/aquatic/waste supply chain optimisation

A number of biorenewable supply chain optimisation studies have been published with majority focusing on pyrolysis, gasification, bioethanol, anaerobic digestion, hydrogen production technologies (Figure 12B) and lignocellulosic feedstock sourced from terrestrial plants and agricultural/forests waste [648]. Aquatic phototrophs and waste value chain planning have attracted more research attention lately.

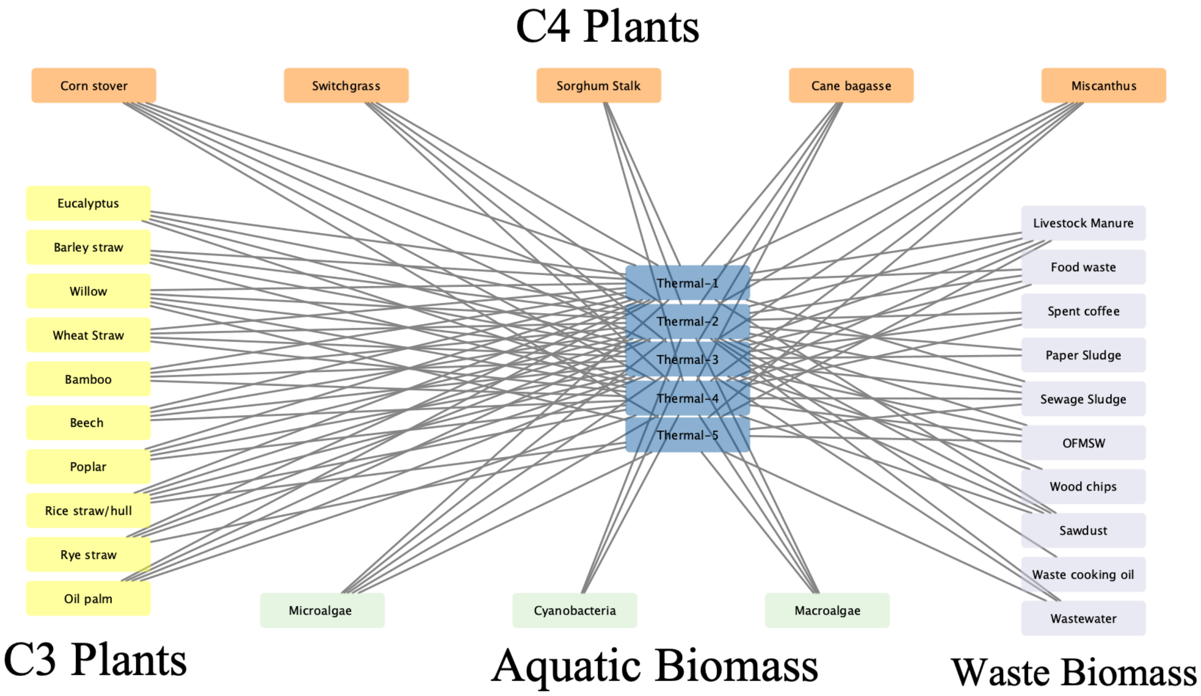
A microalgae based supply chain was modelled using spatial-temporal MILP under both deterministic [649, 650]and robust modes [651] to explore the cost optimal design for biodiesel under supply-demand variance and constraints. Both studies [649, 651] considered the supply chain integration i.e. the wastewater nutrient recovery via algae cultivation and carbon capture and utilisation cycles through microalgae photosynthesis and lipid-extraction and conversion at the refinery. The modelled systems were bounded by the logistics and capacity of the wastewater treatment facilities and pipelines. However, the important spatially-explicit abiotic environmental drivers (solar radiation and temperature) underpinning microalgae photosynthesis were only modelled in the study by Mohseni et al. [651].

Due to the resource complexity and variability at spatial/temporal horizons, waste streams, particularly BFMSW, remain as a relatively untapped opportunity in supply chain optimisation [652]. A multi-objective MIP model was proposed accounting for the overall sustainability of multiple bio-solid waste streams throughout their cradle-to-grave life cycles [653]. The model was configured to consider the mechanical pre-treatment and energy conversation via incineration and anaerobic digestion of MSW, forestry and crop residuals and manure; through system boundary expansion, authors modelled the consequential LCA implications of product substitution on value chain design [653]. Santibañez-Aguilar et al. [654] formulated a multi-objective MILP model to investigate the stream-separated MSW value chain design across-cities to achieve the maximisation of profit and waste recovery. A follow-up study was performed to incorporate the sustainability and safety design criteria in the MILP framework for the strategic planning of MSW supply chains considering mechanical (e.g. recycling) and thermochemical (pyrolysis, gasification, combustion) routes [655]. Waste gas and water streams from various processing industries were addressed in supply chain planning but previous research often focused on single stream management rather than integrated multiple streams with diverse composition. As the diversified waste feedstocks increase the optimisation complexity significantly, bringing multi-scale design problems, which need to consider both superstructure-based process synthesis and value chain planning. Gao and You [656]formulated a life cycle based MINLP model to design the network and management strategy of the wastewater stream from shale gas extraction; a MILP model was proposed to bridge the long-term supply chain planning and short-term batch scheduling problems for water management on shale gas sites considering environmental constraints [657, 658]. Previous optimisation studies addressed carbon capture and storage or utilisation and its integration with algae biofuel value chains, where the spatial carbon sink and source effects over discrete time intervals were mapped [650, 659]. A flare-gas to bio-butanol NLP model was presented to explore the trade-offs between NPV optimal and GHG minimisation, considering the spatially-explicit flare gas streams from multi-sites [660].

Through an overview of biorenewable SC upstream and downstream optimisation studies, a range of promising supply chains have emerged, which deserve future research attention-

- demand-driven SC integration particularly biorenewable products (e.g. pyrolysis bio-crude/bioethanol) with the functional-equivalent petroleum counterparts (e.g. petroleum oil/gasoline) [641];
- supply-driven SC integration for multiple feedstock streams with similar processability e.g. 2G terrestrial biomass integration with 3G algae via HTL;
- centralised and decentralised SC integration for multiple bio-products from diversified feedstock such as the wastewater recovery network design for business parks with effluents from diverse processing industries[661];
- waste value chain design under uncertainty considering the high variance in waste stream composition and supply[662];

- sustainable value chain optimisation for new bio-clusters especially those with higher added-value but lower natural capital inputs such as the microbial single cell protein as resource-efficient food/feed sources;
- Research gaps on value-added biorenewables. As mapped out in



- Figure 11, considerable empirical research has been carried out on novel reaction routes and production pathways, which represents future interests e.g. lignocellulosic biochemicals derived from multi-functioning non-food crops (phytoremediation on degraded land).
- Optimisation studies typically have simplified bio-physical models with fixed exogenous pollution coefficients; knowledge gap emerged on optimisation with interlinked biophysical and supply-demand modelling.

3.6.2 Multi-echelon and multi-scale challenges in biorenewable supply chains

Five interconnected echelons can be generally associated with the biorenewable supply chains – resource supply and collection, manufacturing, storage, distribution and market [645, 663]. As demonstrated in Figure 14, each echelon concerns different decision spaces across temporal and spatial scales. Most long-term strategic optimisation studies reflect the decision region across supply-manufacturing-distribution echelons but in the short/mid-term SC operation, more optimisation effort has been placed on manufacturing decisions with a research gap identified on the operational decisions at supply echelons (e.g. biomass cultivation stage [642]). Supply chain optimisation under fixed echelon settings reflects a rigid network structure, focusing on the logistics, process capacity, transportation mode, inventory control, resource and product flow management. On the contrary, the complexity of the echelons, connectivity between adjacent echelons and functions of nodes are not defined a priori in flexible echelon supply chain design [643]. Tsiakis et al. [664] proposed an MILP framework for flexible multi-product multi-echelon network design with manufacturing, warehousing, distribution and market operated under uncertainty. Lima et al. [665] presented an MILP formulation for optimizing the design of a sugarcane-based bioethanol supply chain, comprising harvesting, production, storage, and distribution, under demand uncertainty. The sugarcane to bioethanol supply chain was also addressed by Wheeler et al. {Wheeler, 2021 #833}.This has been followed by a large amount of literature published on multi-period spatially-explicit models for country/region-level multi-product supply chain design, where the decomposition techniques (e.g. Lagrangean, Benders decomposition, bi-level decomposition) have been proposed to solve the large-scale models and enhance the computational performance [641, 666-668]. The flexible echelon optimisation framework has been widely applied in the biorenewable SC design, enabling systems to consider spatially-explicit natural capital resources (e.g. land use), which are essential ecological drivers interconnected with biomass [669-671]. The fixed-echelon concept was adopted for supply chain transition design to achieve repurposing or retrofitting existing facilities (e.g. petroleum [672] or paper pulp [673] retrofitted to biorefinery).

Multiple spatial and temporal scales need to be coordinated in biorenewable value chain decision-making, ranging from decisions across time steps (hour, day, month, year) to decisions on site location and network at each echelon. As the multi-scale effects relating to the manufacturing echelon have been well addressed in previous reviews [645], our discussion focuses on the supply echelon. At the biomass supply stage, not only strategic planning on land use pattern (e.g. food vs. energy), crop rotation and resource flows, but also the short-term on-farm operational decisions (field operations, irrigation, agro-chemical or fertiliser applications) are important. There have been some attempts to bring a PSE-style optimisation approach to operational decision-making in controlled-environment agriculture (such as [674] and [675]), and mathematical programming also has been widely applied to large-scale long-term agricultural land management; however, the decision variables relating to the operational management of conventional farms are rarely considered [676]. These variables (e.g. fertilization, irrigation, harvesting) not only affect the biomass yield and quality but also are highly related to biogeochemical cycles (e.g. carbon and nitrogen cycling), which impact the environmental performances of biomass and biorenewable systems (e.g. field emissions CO_2, CH_4, N_2O NH_3, impacting eutrophication and global warming) [532]. In addition, biomass supply can be distributed over large spatial areas, where multiple layers are involved e.g. distribution and trading layer, biomass growth layer. The biomass plantation location and sizing selection highly depend on the soil and climate variables (e.g. temperature, solar radiation, soil texture and quality) across spatial scales, which are environmental drivers for biomass yields and influence biogeochemical processes. The response functions of biomass growth and agro-ecosystem C/N cycling to both operational and ecological factors could be captured by first-principle modelling (e.g. biogeochemical simulation) and incorporated into optimisation using surrogate models or discrete scenarios.

Surrogate modelling can be traced back to the end of 1980s. New research areas emerged to apply response surface model (RSM) to computer experiments and approximate functions to model and optimise complex systems. To reduce computational complexity using simulation, a ‘black-box’ approach can be applied to use the original simulator as a source of computational experiments to generate data points. The sampled input-output data can be fit into surrogate functions. Different sampling techniques have been explored such as Sobol’ sequences techniques [677], which provide good input space coverage in a minimum number of samples. Research also covered different RSM methods including noninterpolating (i.e. least squared error of some predetermined functional form) and interpolating (pass through all points e.g. Kriging interpolation) approaches. As applied in previous research [678], Kriging interpolation method models the underlying function as a stochastic process and has the benefit of quantifying the uncertainty in the surrogate model predictions. However, the requirement for the inversion of a covariance matrix in the model formulation means high-dimensional problems can become computationally demanding. Alternatively, artificial neural networks (ANNs) or other metaheuristic algorithms can correlate multiple input-output relationships and derive a good degree of accuracy [679, 680]. Recent advances in surrogate-based optimisation has been covered in a comprehensive review by Forrester and Keane [681] and surrogate-based optimisation advances in PSE is reviewed by Bhosekar and Ierapetritou [682].

Despite the wide applications of surrogate modelling in modular flowsheet optimisation of chemical processes[683], its application in soft-linking first-principle biogeochemical models with mathematical optimisation remains unexplored. By applying such meta-model approach, the derived surrogate models are expected to represent the accuracy of first-principle modelling and project the C/N cycling over continuous time. Integrating surrogate functions into whole system optimisation, the date-driven modelling techniques could enable computationally tractable decision based on accurate projection of environmental process over temporal and spatial scales. Such data-driven optimisation can reflect the implications of the temporal and spatial-scale decisions on the wider biorenewable supply chain design.

Overall, the biorenewable complexity at multiple scales may result in large scale optimisation models thus the future research challenge in this highly cross-disciplinary field lies in the trade-offs between optimisation solution quality and computational complexity.

3.6.3 Natural capital and built environment resources

Biorenewable supply chains are interconnected with natural capital (e.g. land, water, air) and built environmental resources (e.g. electricity, infrastructure) and constrained by their capacities (e.g. land availability and electricity generation capacity) across spatial and temporal scales. These not only form the optimisation model exogenous constraints but also underpin the resource competition issues between multiple sectors (e.g. food vs. bioenergy, biorenewable vs. petroleum). The majority of the optimisation models define biomass availability as given parameters independent of natural capital resource e.g. land [684] and water [685]. Relatively different, few studies considered biorenewable value chain competition and decision variables on land use [188, 686-688]. Cobuloglu & Buyuktahtakin [689] formulated a deterministic MILP model to explore the arable land decisions on a switch grass-based biofuel and food competition at different spatial scales; the authors further proposed a stochastic MIP model to optimise food-biofuel competition considering the variance in biomass yield and price[690]. A Stackelberg–Nash game model was developed to study the effects of land use regulations on the food and biofuel balance[688]. Čuček [687] developed a multi-period MILP model to optimise the total land areas devoted for biofuel and food demands.

However, not all the land is suitable for biomass production due to soil and typographic constraints. Two land taxonomy systems arise here which are related to biomass optimisation problems – soil type and land cover. The former refers to different sizes of mineral particles (clay, silt, sand) in the soil samples, varying with countries e.g. the UK soil taxonomy with 10 major groups [691]; whereas the latter represents the observed biophysical cover on the earth's surface[692], which has been developed at national or regional level e.g. UK land cover map [693] and EU CORINE (coordination of information on the environment) land cover classification [694]. Soil type as an important environmental driver has been taken into account in various biogeochemical models; spatial land cover and slope layers have been incorporated in national SC optimisation models to identify the optimal site location for PV water pumping systems in China [695] and to design UK spatial-temporal bioenergy supply chains accounting for the trade-offs of cost optimal and environmental targets [696, 697]. The UK national bioenergy model ETI-BVCM [696, 697] was formulated as a MILP optimisation, where the GHG and biomass yield derived from empirical models were embedded and initial land cover GIS layers were included; this model was further extended to incorporate spatially explicit land competition between bioenergy and non-energy systems over time at different land types (arable, grassland, forestry land etc.) and the ecosystem services impacts in response to the decisions on land use changes [188]. However, an overarching framework to integrate first-principle biogeochemical models (e.g. DNDC, ECOSSE) with multi-scale multi-echelon optimisation has not been explored and represents a promising research direction; this approach brings soil biogeochemical cycles and soil-plant interaction into the land use decision framework, which underpins the terrestrial biomass-dependent biorenewables and enables supply chain optimisation to account for soil and other environmental variables.

It is particularly interesting to model a range of land-use mitigation strategies e.g. land sharing and sparing schemes [426, 698] in the optimisation to shift the land competition to land-use integration or reconfigure the biorenewable systems via sustainable agriculture intensification [698]. In addition, land-sparing and land-sharing have emerged as alternative strategies to achieve both production and biodiversity conservation. [699]. Land-sparing involves specialization of land uses, setting aside lands for conservation and implies agriculture intensification somewhere else to compensate for a reduced area availability [700]. In contrast, land-sharing is defined as making production lands more conducive to biodiversity conservation to integrate food production with ecosystem services [700].Both strategies require a financial concession to conservation (i.e. opportunity cost), thus it is essential to identify the cost-effective strategy for ecosystem services conservation [701]. Alternative land-sharing and land-sparing strategies, including mixed strategies, have been evaluated by integrating multi-objective integer programming with conservation planning in previous research [702].

With the increasing concerns on the ongoing global degradation of natural capital, the competition issues on other resources especially water, and interaction of natural landscape and environment with biorenewable products deserve future research efforts. Substantial amounts of water are used and waterborne pollutants are discharged at multiple supply chain echelons (biomass cultivation, biorenewable conversion). The water-biorenewable nexus have been considered in several optimisation works. By bringing the water footprint into the objective function, Garcia and You [703] proposed a multi-objective MILP model for water-biofuel network design. Similarly, water resource use, regional watershed management and wastewater discharge were considered in the design criteria in the biorefinery supply chain model proposed by López-Díaz [704], where the interaction of a watershed with the entire supply chain was characterised using material flows.

Another important natural capital is carbon dioxide assimilation. In contrast to linear supply chain optimisation problems, the carbon circular and waste-based biorenewable systems lead to closed-loop supply chain design. Closed-loop supply chain (CLSC) has been of great interest for mathematical modellers; an up-to-date review on the CLSC research can be found in [705-707]. The strategic (e.g. location), tactical and operational (e.g. inventory) decisions at multiple echelons have been modelled in multi-objective CLSC research considering social-economic-environmental criteria under uncertain environment with varying infrastructure, demand, costs, recycling and social impacts[708-712]. In contrast to the centralised supply chain design strategy, Nash equilibrium framework was adopted to formulate decentralised stochastic CLSC under demand and return uncertainties [713-715]. Applying CLSC design in biorenewables, the closed-loop biogenic carbon refinery supply chains (e.g. bio-based recyclable PET bottle) can be simulated to explore the potential contribution of such circular biorenewables to the global climate change mitigation.

Natural capital underpin ecosystem services, which are delivered to human wellbeing through the flows and interactions between natural capital assets, built capital (built environment) and human capital assets (people and society). Previous research has elaborated the interconnection between natural capital and built capital assets by examining ecosystem services trade-offs [716]. The evolvements of existing infrastructure and resource flows as part of the built environment (e.g. transportation, energy, waste treatment and water supply) can be defined as exogenous but uncertain parameters in optimisation models. Two types of supply chain risks arise from the uncertainty in built environment resources and infrastructure i.e. operational or disruption risks. The former refers to the fluctuation in the biorenewable supply chains due to the uncertainties in the supply and demand of the built environment resources; while the latter is associated with the external interruption in built environment (e.g. infrastructure failure) caused by natural or artificial extreme events (e.g. policy intervention, flooding, hurricane)[717]. The capacity, demand and interdependency of these infrastructures under future uncertainty can be captured *via* system simulation e.g. the UK ITRC national infrastructure modelling platform based on a system of systems approaches [718]. By adopting simulation parameters as exogenous boundary conditions, scenario-based stochastic optimisation can be used to explore biorenewable SC decision-making under built environment uncertainties and risks [719].

3.6.4 Cooperative vs. non-cooperative supply chain strategies

Across five supply chain echelons, multiple interactive nodes are involved in the supply chain decision-making, where the nodes can compete in either cooperative or non-cooperative fashion. Unlike the centralised optimisation approach, competitive supply chain problems represent a decentralised system with each decision-maker taking their own strategies, which often conflict with each other. Different negotiation scenarios have been studied in optimisation - cooperative games with competition between groups of players [720], non-cooperative games and standalone cases [721]. A scenario-based dynamic negotiation model was formulated by Hjaila et al. [721] , which enables leaders and followers to participate in production-distribution decentralised networks and explore both cooperative/non-cooperative games under uncertainties. The cooperative mode was also modelled for decentralised water-use network [722]. In comparison, the non-cooperative game with n nodes underpinned by the Nash equilibrium concept [723, 724] is the most widely used methods of predicting the outcomes of a strategic interaction. Nash-type mathematical programming proposed by Gjerdrum et al.[725, 726] was a new method to model the inter-organizational cooperation and information sharing mechanisms as well as profit distribution amongst nodes under a competitive environment. The authors formulated a deterministic MINLP model to determine the optimal transfer prices for n-node supply chain; MINLP functions were linearised using logarithmic differentiation and approximation. Yue and You [727] further studied the profit allocation in a non-cooperative supply chain by optimising transfer prices and revenue sharing, where a branch-and-refine algorithm developed by You and Grossmann [728] was applied to solve the model. Later on, the same authors proposed a bi-level optimisation model to explore competitive biofuel supply chain decisions following the Stackelberg leader–follower game theory [729]. To model the uncertainties in both leader and follower's problems under a non-cooperative and non-zero-sum Stackelberg game, Hjaila et al [730] proposed an integrated framework to solve the Stackelberg game by a MINLP tactical decision model and consider the competition between Stackelberg nodes and third parties in a Nash equilibrium model. By using Monte-Carlo simulation, the authors derived the pareto-frontier win-win solution set under uncertain competition conditions from both leader and follower perspectives. The Nash equilibrium state was also explored in the closed-loop supply chain optimisation problems using deterministic optimisation [715] and a stochastic model considering the demand and return variance [713]. CLSC Stackelberg leader–follower game was formulated as a multi-objective optimisation model and solved using genetic algorithms [731].

These game-theory models were mostly based on fixed supply chain echelon models with exception of [729] and. [732], where the flexible echelon based supply chain models were constructed with binary variables determining the candidate site selection and biorefinery capacity levels. Although land use competition has been recognised as a critical issue, facing triple challenges amongst food, bioproduct, and environmental conservation, only the Stackelberg–Nash game model formulated by Bai et al. [732] considered the strategic decisions on candidate biorefinery locations and land allocation for food and bioenergy crops while taking into account the non-cooperative gaming behaviours. The model was further enhanced by the authors [733] to simulate how the farmland use policy regulates food-biofuel production. However, as discussed in the previous section, interaction of land with biomass is dynamic, varying with land type. Thereby, one of the major challenges lies in how to simultaneously model the competitive n-node game and capture the type-specific natural capital allocation decisions for resource-competing biorenewable supply chains at fine spatial and temporal scales. An optimisation framework was proposed to incorporate crop simulators and multiple echelon supply chain competitive games to achieve the equilibrium solutions for multi-players (feedstock suppliers, existing industries, centralised/decentralised biorenewable operators, investors, and policy-makers)[734]. The land use allocation at four land types (arable, forestry, grassland and abandoned) for resource-competing systems and closed-loop waste recovery were modelled as decision variables; such modelling approach could be extended to simulate other innovative sectors under circular economy.

3.6.5 LCSA optimisation incorporating wider ecosystem services

By bringing life cycle thinking into the decision-making framework, the PSE research community proposed a life cycle optimisation (LCO) methodology and applied it to biorenewable multi-scale design problems [596, 605, 646, 735-737]. Earlier LCO models focused on the trade-off between economic and environmental criteria in biofuel supply chain planning from attributional perspectives over entire life cycle [738] or cradle-to-gate life stages [739]. Čuček et al. [653] considered sustainability in three pillars and extended the attrtibutional LCO framework to social dimensions, which was followed by the multi-criteria models presented by You et al. [737] and Miret et al. [736]. They proposed to model direct and indirect job creation as social performance indicators, including the employment impacts reflected in biomass supply chain operation and infrastructure construction phases and the jobs resulting from local economy change throughout the biomass cradle-to-grave life cycle. The activities in local micro-economy concerning multiple sectors and nodes were quantified using an input-output modelling approach [737]; in particular the ‘induced’ employment opportunities [736] resulted from the economic activities supported by the household expenditure spent by biorenewable sector-related employees have multiplier effects. Such effects in fact reflect the consequential impacts although were not discussed by the authors. Until recently, the consequential LCO concept was formulated as a global MINLP problem and introduced by Gong and You [605] to capture the changes to the upstream and downstream processes as a consequence of trade-off design for a algal biodiesel production network.

Landscapes generate a range of ecosystem services; the type, magnitude, and relative mix of services provided by ecosystems can vary with management interventions, where the ES trade-offs could occur at various spatial and temporal scales [740]. Although the importance to incorporate such ES into decisions at international, national, local and corporate scales is increasingly recognised [393, 394] especially for the natural capital-dependent biorenewables, their value is often overlooked in resource or biorenewable supply chain planning [395]. By introducing the location-independent regulating ES impact factors into their MIP model, Hanes et al. [741] formulated an optimisation model to optimise the ES use sustainability with supply and demand balance accounted for. In this study, climate-regulation and air quality regulation impacts induced by farmland use change were quantified as CO_2 eq and NO_2 eq where the farming activities and carbon nitrogen balances were captured using a process-based model WinEPIC but soil drivers were excluded by assuming homogeneous soil type. Kovacs et al. [742] explored the implication of ES conservation policies on the trade-offs between ES and agricultural economic return optimal for landscape management. In a proposed bioenergy value chain optimisation framework [188], spatially-explicit provisioning ES relating to the food bioenergy, livestock production from dedicated and competing land resources were considered quantitatively as is the regulating ES; a semi-quantified matrix was introduced as a synthetic measure to account for biodiversity and other ES as a consequence of land use transition across different land types. Under this framework, the authors proposed to implement quantitative approaches based on provisioning, regulating and cultural ecosystem services at various spatial and temporal scales to optimise the ES trade-offs for the bioenergy supply chain design. An interesting yet unexplored direction is to bring the ES supply-demand mitigation strategies into the LCO framework e.g. multi-functional landscape planning [415], phytoremediation or bioremediation on degraded land.

Overall, life cycle underpinned optimisation offers a promising framework to inform decision-making towards biorenewable sustainability; several interesting yet challenging research directions lie in the methodological exploration for consequential LCO of closed-loop biorenewable supply chains (e.g. biogenic CO_2 based recyclable plastic), spatially-explicit ES optimisation linked with eco-informatics and ES databank, LCO with wider quantitative social dimensions. These challenges can only be addressed via collaborative research efforts to bring together multidisciplinary expertise across Ecology, PSE and Social Sciences.

3.7 Multi-criteria challenge and supply chain simulation

3.7.1 Multi-criteria decision-making

Under each biorenewable supply chain echelon, multiple nodes are involved in the decision-making process, thereby the biorenewable system may lead to many-objective large scale optimisation problems. The term ‘many-objective’ refers to the optimising systems with four or more design objectives as introduced by Fleming et al.[743], which could be expressed as –

$$\text{Min}\, f(x) = \{f_1(x), f_2(x), \ldots., f_k(x)\}\ \ x \in \mathbb{R}^n$$

$$f_{k\in[1,m]} := \mathbb{R}^n \to \mathbb{R}$$

Where the parameter vector $x \in \mathbb{R}^n$ is subject to boundary constraints, forming the feasible space. The vector function f maps the objective space. The PSE literature reviewed above represents multi-objective optimisation problems with 2-3 design criteria, which are often resolved using *a priori* or *posteriori* algorithms to find a whole set or a subset of non-dominated solutions. The former involves decision makers prior to the optimisation, considering multiple attributes in the form of a weighted sum in a single objective function, but it does not reveal the Pareto front supporting an informative decision making process and weights introduced for each criteria may change the dominance structure of the multi-objective problem and hinder the discovery of global optimum solutions[744]. The latter provides a set of solutions based on the trade-off between conflicting objectives and articulates the decision-makers preference in searching optimal solutions in the objective space. However, because the complexity of multi-objective problems increases sharply increases with the number of objectives,{Weidner, 2022 #832} more than three conflicting objectives in *posteriori* approach are regarded as computationally intractable. Indeed, Weidner et al. {Weidner, 2022 #832} note that optimizing over all nine PBs would be highly computationally demanding. Instead of aggregating or omitting the objectives, an alternative approach is to reduce the objectives without losing information. Guillén-Gosálbez [744] introduced a *posteriori* algorithms based on a branch and bound technique to reduce the Pareto objective space; via iteration, a set of solutions will be derived until the termination criteria are satisfied. Different from both approaches, interactive optimisation represents a human-in-the-loop approach (Figure 14), aiming to turn efficient optimisation methods into effective decision-making tools [745]. The interactive methods articulate the dynamical preferences of multi decision-makers based on their gradually-built understanding of the optimisation topology and enables the solution search to be progressively refined and directed towards the regions of interest; thus this approach can outperform a black box optimisation methodology [746]. Evolutionary algorithms e.g. genetic algorithm[747], particle swarm optimisation (PSO) [748] and other artificial intelligence (AI)-based methods e.g. fuzzy chance-constrained programming [749] have attracted great research attention; they were applied to solve many-objective engineering design problems including hybrid electricity and gas network [750],renewable energy scheduling [751], collaborative water supply planning [747], and biochemical system design [752]. Research efforts has been also placed on interactive methods for multi-objective MIP; published description of methods on the interactive MIP can be found in the review conducted by Alves and Climaco [753].

Visualisation of high dimensional (four or more) objective or decision spaces is another challenge. Pryke et al.[754] presented a heatmap visualisation method and compared it with two other approaches (self-organising map and distance and distribution charts); a heatmap-based user interface was introduced to interactive PSO models [755]. Inselberg [756] proposed a parallel coordinates approach to visualise non-dominated candidate solutions; this method was combined with evolutionary algorithms [743] e.g. web-based PSO-based interactive many-objective optimisation and a scatter-plot to plot out any two parameter or objectives to facilitate decision-makers progressively articulating design preference [757]. Despite the fact that interactive optimisation has been successfully applied to engineering design e.g. aeronautics, the methodology and application research on many-objective biorenewable optimisation is still challenging due to the multi-scale, multi-echelon complexity, resource-competing issues concerned and the interaction with wider natural and built environments.

3.7.2 Stakeholder interaction and policy intervention

Amongst multiple decision-maker groups, governmental agencies, policy-makers and regulators play significant roles in the new biorenewable technology and supply chain deployment. The optimisation studies reported in the literature often focus on the market players but considered policy instruments as exogenously parameters (e.g. carbon trading price). It is important to account for the policy-makers in the modelled system as decision-makers, bring the governmental economic (e.g. budget) targets into the objective space and their deployment policy variables into design space. This could be achieved by introducing the policy stakeholders as key market regulators in the models, which enables them to explore the strategic planning options defining the macro economy boundary conditions, setting rules and implementing policies. Based on the IRN21, IPCC and IEA renewable energy deployment reports [758-760], different deployment policies could be summarised and expressed as several key schemes (please see related material in the Supplementary Information SI-5) [761]. By bridging the dialogue barriers and engaging the stakeholder groups throughout model development, the academic community could scope the model functions from different user perspectives and formulate optimisation problems with useroriented architectures. Such a modelling strategy could more effectively inform the decision-making process to ensure the solutions are applicable for read-world problem-solving.

In addition to policy instruments, the governance and supply chain structure, node interaction and behaviours have proven to be important factors influencing bioproduct technology deployment [762]. These can be addressed by using agent-based modelling (ABM). ABM adopts a bottom-up approach considering each node to react autonomously and cognitively to environmental change[406]. It has been applied to investigate agriculture-level decision making [406, 763] as well as biofuel supply chain design [549, 764-767] and carbon emission trading schemes [768]. The decisions and interactions of each node can be modelled simultaneously with solving the multi-scale design problems by using ABM and enabling dynamic simulation-optimisation loops in a complex system analysis. Singh et al. [764] combined ABM with a genetic algorithm to investigate how the node decisions at biomass-supply echelon under a food-biorefinery competing market affect corn price and further influence the biofuel supply chain design. Delval et al. [769] formulated an ABM simulation-optimisation framework to simulate the node interaction at multiple levels (vertical and horizontal) based on behavioural diversity and optimise the sugarcane supply chain strategic design and each node’s tactical planning simultaneously under the demographic evolving context over five decades in South Africa. Via soft-linking ABM with LCSA and ecosystem services, research has been carried out to evaluate the implications of farmers’ decisions on the greenhouse gases and ecosystem services performances of bioenergy supply chains [406, 770]. Robust optimisation offers an alternative approach to supply chain optimisation, treating exogenous decisions, such as demand, as uncertainties [771].

Employing systems approach, the simulation-optimisation-evaluation loops offer powerful modelling tools to explore the multi-scale, multi-echelon biorenewable system design space, interconnected with natural capital and built environment and accounting for multiple criteria from different decision-maker perspectives. However, all models introduce some form of approximation, uncertainty or assumptions. Citing George E.P.Box [772]and John Sterman [773] ‘all models are wrong.’ Biorenewables have inherent system complexity, which cannot be artificially divided into sub-systems or segments; thereby, it is very important to take a whole system approach and break down the disciplinary barriers. Forming a systematic cross-disciplinary modelling framework (Figure 14) offers a promising way to merge multi-level research questions and capture the dynamic interactions of biorenewable system components as well as their inter-linkage with the wider ecosystems, natural and built environments.

3.8 Optimisation under uncertainty

Following the taxonomy proposed by Piedro et al. [774], this section addresses optimisation under uncertainty from three perspectives – uncertainty sources, problem types and modelling approaches.

Differing from petroleum based counterparts, biorenewable systems particularly those based on the terrestrial and aquatic phototrophs are highly dependent on the environmental and ecological drivers (e.g. climate, soil, water, vegetation). Thus, there are significant uncertainties e.g. feedstock quantity quality and seasonality, across the systems at multiple levels due to the temporal, spatial, environmental and socio-economic uncertainty and variance, which can be categorised following temporal-scale. As summaries in Table 7, in addition to the uncertainty associated with supply chain (demand, supply and process) [774], uncertainty is also associated with exogenous factors due to environmental or socio-economic interventions (e.g. policy). The probability distribution of the ecology or environment related exogenous factors can be estimated either based on historical data (e.g. extreme events such as flooding earthquakes or meteorological data) or computer simulation (e.g. crop yield projection [365]); whereas the probability distribution of exogenous socio-economic drivers (e.g. market demand, technology evolution) could be obtained from system dynamic or economic model forecasts. Often, an optimisation problems with discrete (finite) probability spaces are derived for biorenewable systems particularly those combining multi-scale uncertainties which could result in intractable nonlinear problems if assuming continuous distributions [775].

Previous studies proposed the classification of uncertainty modelling approaches into four groups [774, 776] – analytical methods (e.g. robust optimisation, stochastic programming), simulation methods (e.g. discrete-event simulation, Monte Carlo simulation), artificial intelligence-based model (e.g. fuzzy programming, evolutionary programing, genetic algorithm), hybrid model (integration of analytical and simulation methods e.g. stochastic dynamic programming [777]). As recommended by Piedro et al.[774], analytical approaches generally can be adapted to manage the random uncertainties while the simulation and AI-based models can be applicable to capture complex system behaviours. Specifically, stochastic programming presents a suitable method for biorenewable problems with uncertain parameters represented as a set of discrete scenarios with probability levels or a continuous projection ranges (e.g. temperature, yield); while robust optimisation could be suitable for the cases where the uncertain parameters are represented as uncertainty bounds (e.g. land availability) [778].

Via literature review, the following points emerged which highlight potential opportunities (see Supplementary Information SI-6) -

- planning on upstream (cultivation [779], production [780]), downstream distribution[781], and demand side [782].have been modelled under uncertain decision-making environment. The supply and demand flows and their market prices were widely addressed as uncertainty sources but process (e.g. technology evolution [778]) and other factors (e.g. policy, biomass quality[780], climate [783], land availability [784, 785]) were not commonly included;
- uncertainty-based optimisation studies focused on supply chain planning with very little research concerning the process synthesis [786-788]; planning across multi-period horizons is concerned in several studies e.g. [651, 779, 789, 790] but the incorporation of tactical, strategic, operational planning simultaneously in an uncertain decision-making environment is rarely investigated [786];
- multiple biorenewable supply chain integration, resource-competing issues (food vs. biofuel), process repurposing and multi-echelon supply chain design under uncertainties still remains unexplored;
- the analytical and simulation methods along with fuzzy programming were commonly adopted approaches in previous research to solve the design problems whereas other AI-based models e.g. meta-heuristics approach are worth future research efforts;
- Benders decomposition was widely applied to solve the scenario-based stochastic optimisation programs but other applicable methods e.g. progressive hedging algorithm have not been explored in multi-stage stochastic optimisation [774, 775].
- LCA-based optimisation under uncertainty was presented to solve multi-criteria design problems for biomass and biorenewables e.g. [790-792], but social performance was often overlooked (e.g. job creation) [793].
- Our review confirmed the statement of Govindan et al. [775] that the systematic comparison between different modelling approaches deserve further research attention.

Linking uncertainty concepts with the biorenewable system design, three performance indicators emerged - robustness, responsiveness and resilience [794]. The solution robustness determines the extent to which the system can carry out its functions under a variety of future scenarios; as proposed by Klibi et al. [794] weighted scenarios based on random, and worst discrete events should be integrated and accounted for in stochastic programming to measure the robustness. System responsiveness provides a matrix to evaluate how the system performs in response to short-term variations in system inherent operational risks (fluctuation in supply and demand)[717]; resilience evaluates the system capacity (e.g. structure and resources) to quickly recover, adapt and grow facing the unexpected external disruption risks caused by natural and artificial disasters [3, 717, 794]. Deterministic optimisation approaches applied in majority of biorenewable systems are not capable of capturing these indicators but uncertainty is particularly important for biorenewable system design, which faces higher levels of operational and disruption risks than petroleum counterparts (e.g. feedstock supply interruption due to natural disaster).

Few studies addressed this topic. Pishvaee et al. [795] presented a robust linear optimisation model to address multi-echelon logistic network operational design, considering conflicting cost and responsiveness objectives. Network responsiveness was also concerned in closed-loop supply chain decisions under uncertainty [796-798], where metaheuristic approach (fuzzy genetic programming, PSO) were proposed to solve the optimisation problems. At the manufacturing level, responsiveness is also important design criterion in particular for assemble-to-order production models [799]. The resilient supply chain as an emerging field has not attracted attention until very recently, when pre-disaster planning and infrastructure retrofit decision elucidated the concerns on resilience [800-802]. Huang and Pang [719] proposed a multi-objective stochastic MIP model for biofuel infrastructure design; the model accounted for the conflicting cost and four resilience measures i.e. robustness, rapidity as the inherent resistance measures in the infrastructure change to extreme events, and redundancy and resourcefulness as the system stability indicators to recover functionality from the supply/demand changes. However, the multi-scale, multi-echelon responsiveness and resilience in biorenewable system design has not yet been explored; by integrating the risk mitigation and resilience-building measures into the stochastic spatial-temporal optimisation models, this complex area presents a potential future research direction.

Table 7 Overview of the optimisation under uncertainty

STAKEHOLDERS	SHORT-TERM OPERATIONAL UNCERTAINTY	MID-TERM TACTICAL PLANNING UNCERTAINTY	LONG-TERM STRATEGIC UNCERTAINTY
BIOMASS CULTIVATION AND COLLECTION	• biomass yields due to meteorological and soil condition change • agrochemical supply • biomass demand	• new genotype • new crop introduction • field management • facility interruption due to extreme events	• policy change, • land use change • cooperative or non- cooperative (e.g. contract) strategy of other enterprise across supply chains
BIORENEWABLE TECHNOLOGY OPERATION	• Batch and transport scheduling • Biomass price and quality uncertainty • Biorenewable demands uncertainty • Operational condition	• capacity planning • inventory management • pollution control • seasonal biomass availability • market uncertainty • policy change • facility interruption due to extreme events	• Investment strategy and location selection • customer preference change • policy change • market and global trading • technology evolution • built environment (e.g. energy-water infrastructure).
CURRENT PETROLEUM INDUSTRIAL SECTORS			• Reconfiguration and expansion of existing facilities, process repurposing due to uncertain biorenewable sectors.
DISTRIBUTION CENTRES	• inventory management due to the unpredictable supply and demand; • Transportation scheduling		• contract decision affected by the uncertainties in market and other stakeholders involved in the supply chain.
GOVERNMENT, POLICY-MAKERS AND REGULATORS			• policy and subsidy strategies due to unpredictable weather, environmental change (e.g. climate change) and natural extreme events (e.g. flooding).
FINANCE SYSTEMS		• Investment led by the changes in market supply-demand and government policies and weather and environmental unpredictability.	

3.9 Technology learning curves

Understanding how technology performance evolves over time is the key for multi-level decision-making on biorenewables and underlines the projections on costs of achieving sustainability targets. Different hypotheses on endogenous learning-diffusion have been proposed and tested in previous research e.g. Moore's law [803], Wright's law [804], Goddard learning curve [805] , SKC curve [806], Nordhaus logarithmic function [807] (equations presented in Supplementary Information SI-7). Previous statistical analyses with tests of over 60 technologies demonstrate Wright's and Moore's laws outperforming other approaches [808]; the authors concluded that information technologies tend to follow the Wright's law whereas Moore's law represents better the patterns of other technologies like fermentation although with slower improvement trends. Wright's law generalised as an experience curve [809] $Y_t = a\mathrm{X}_t{}^{b}$, represents the 'learning-by-doing' phenomenon observed in the manufacturing industries and forecasts the unit costs Y_t at a cumulative production level X_t over time t. Parameters a and b denote the unit cost of the first production unit and the rate of cost reduction, respectively [810]. Extending to a class of technologies, e.g. energy power plants, the independent variable X_t reflects all experience factors affecting the cost trajectory [811]. It is the most often adopted learning function in energy systems including bioenergy, biofuels [812-814]. One factor experience curves were further expanded to multi-factor models, component-based learning curves (see Supplementary Information SI-7) to account for other endogenous technology factors (learning-by-researching, knowledge shock etc.) and exogenous changes [809, 815-817]. In particular the component-based learning hypothesis has been further expanded to model design complexity (interconnectivity of sub-components) [816] and entire supply chains with decomposed technology learning [545], where four types of learning effects were differentiated i.e. endogenous labour-associated learning, endogenous input learning, exogenous supply chain learning (labour and input). Such expansion and decomposition enable system optimisation models to capture the learning implications for economic and environmental objectives [545, 546].

Although the exogenous learning curve-derived parameters were introduced in previous studies e.g. bottom-up model MARKAL and TIMES (The Integrated MARKAL–EFOM System) [818, 819], the deterministic optimisation approach is not capable of capturing the uncertainty associated with technology evolution. Stochastic and dynamic programing are promising methods to incorporate technology learning curves into optimisation frameworks [813, 820-822]. In both methods, two types of variables can be distinguished–decision variables controlled by decision-makers and state variables used to describe the mathematical state of a dynamic system at stage n, which is indirectly determined by decision variables at the previous stage $n-1$ and influence the decision variables at a later stage $n+1$ [813]. Chen et al. [820] used exogenous approach (i.e. externally determined boundary conditions) and adopted stochastic optimisation with discrete scenarios to model the cost reduction in response to evolving biofuel technologies. An exogenous approach has been also applied in the stochastic MILP study on carbon capture technologies where the future cost parameters were determined by Wright's curve [822]. A similar method was used in renewable energy production network design by Cong [823]. Chen et al. [813] later explored endogenous methods applying multi-stage dynamic optimisation to build a learning-by-doing function in the model and investigate from a regulator perspective how the cumulative production interacts with the inter-temporal strategic planning. They set the cumulative production of 2G biofuel at each stage n as a state variable, which determines the unit cost of the given biofuel following Wright's law, and defined the production of other competing fuels as decision variables; the model was lower bounded by the total fuel demands. Stochastic and dynamic programming can be further expanded to 1) incorporate the multi-factor environmental learning curves e.g. carbon intensity abatement and derive the trade-off solutions between conflicting objectives; or 2) formulate the value chain learning in the time-dependent system design from both centralised and distributed perspectives (e.g. equilibrium system with competing nodes). The accuracy and representativeness of the learning coefficients underlying the optimisation model is the key for obtaining robust decision-making support, which could be estimated using various methods e.g. PSO algorithm [824]; thus how to integrate the learning curve simulation of biorenewable technologies with multi-scale decision-making within an dynamic optimisation framework worth research efforts. However, this highly dynamic topic remains unexplored.

3.10 Modelling research frontier beyond state-of-the-art

Overall, terrestrial, aquatic biomass and waste resources can be converted into value-added biorenewables, which are regarded as highly complex systems of flows that are subject to nonlinearity, sensitivity and uncertainty. Take terrestrial C3/C4 higher plant species as an example. Their carbon sequestration and composition are regulated by physiological traits, photosynthesis pathways and environmental variables. Thus the resulting chemical compositions vary with species and show spatial-temporal variation, which further affect downstream biorenewable manufacturing. Decoupled modelling approaches (e.g. first-principles modelling, empirical modelling) have been developed to advance fundamental understanding and design new solutions to biorenewable subsystems. However, this increases computational complexity and brings challenges to model the whole biorenewable system in a unifying framework.

State-of-the-art computational methods have been reviewed in this study. Coupling these modelling methods leads to a multi-scale modelling framework (Figure 14), which offers a potential approach to tackle the biorenewable system complexity. Such multi-scale modelling framework represents a highly cross-disciplinary approach, which can link inherently the biorenewable subsystems (natural capital resources, agro-ecosystems, refinery manufacturing, waste and pollutant fate and treatment, transport and network). Specifically, metabolic modelling can advance the understanding of the phototrophic microbial cluster in biological carbon sequestration and cycling and catalyse aspiration towards photosynthetic microbial refineries. Biogeochemical models combined with process simulation enable to simulate agro-ecosystem complexity (e.g. biogeochemical cycles and environmental interaction with higher plant species) and biorefinery processes and compute resource flows and carbon and nitrogen transport and transformation across biorenewable whole systems. Coupling LCSA, ecosystem services and PB framework not only provides quantitative approaches to evaluate the holistic sustainability of biorenewables, but also offers a systematic tool to investigate the implications of biorenewable on wider ecosystems and planetary boundaries. Further, the GIS-aided model integration brings multi-spatial scales into the framework and links spatially-explicit ecosystems with biorenewable manufacturing; whereas the advanced mathematical optimisation research offers a way to design complex biorenewable systems with conflicting decision criteria. Overall, our literature review suggested a range of emerging modelling gaps in multi-scale biorenewable systems modelling, which represent frontier research directions beyond the state-of-the-art and can be summarised as follows–

- Coupling data advances (remote sensing) and modelling (e.g. machine learning, GIS-aided tools and biogeochemical simulation) to understand availability of terrestrial, aquatic biomass and waste resources and project their chemical composition in response to environmental variables, socio-economic and demographical changes.
- Simulation and design of integrative CO_2 biorefinery based on empirical research advances on designed versatile microbial consortia and technologies to convert higher plant species to value-added biorenewables.
- Methods to optimise biorenewable recovery from waste resources to transform CO_2 from a pollutant to a resource and converge zero-carbon technologies and resource-circular biorefining towards a zero-waste, zero-pollution biorenewable system.
- Approaches to tackle the varied non-linearity and sensitivities of numerical models and combine different computational methods and models into an integrative framework.
- Mathematical modelling approaches to bridge ecosystem and biorenewable manufacturing design spaces and capture dynamic feedbacks and interdependencies (e.g. interdependence of biorenewable and natural capital) to enable computationally trackable optimisation from whole systems perspective.
- Mathematical optimisation development to optimise flows and decision spaces across spatial and temporal scales e.g. bridge agricultural operation scheduling and value chain planning.
- Optimisation framework development to design biorenewable flows and interaction with natural capital and built capital assets to achieve ecosystem services trade-offs.

- User-interactive optimisation model with module-oriented architectures and preference-learning interface to enable decision-makers to articulate the preferences of multiple decision criteria, define the feasible spaces and feedback objectives and decision spaces.
- Mathematical theories and techniques for improving the model performances (e.g. precision and responsive decision) in response to big data advances e.g. trade-offs between solution quality and model complexity reduction.
- Advanced cross-platform life cycle optimisation software underpinned by collaborative data value chains and server platform to support real-time database update and responsive decision-making.
- Stochastic optimisation with risk mitigation and resilience-building measures to optimise multi-scale, multi-echelon biorenewable supply chain under uncertainty.

4. Final remark

Increasing environmental stress coupled with expanding population bring challenges to sustainable development of ecosystems and wellbeing. The transformation to a resource-circular bio-economy offers a mechanism to tackle environmental changes and degradation. As advanced bioeconomy components, biorenewables are expected to play significant roles over the next decades. This comprehensive review reflects the empirical advances in upstream and downstream processes and highlights the system perspectives of biorenewable, which are subject to nonlinearity, complexity and variability. From a whole systems perspective, biorenewables feature biogenic carbon flows and resource circularity. Upstream phototrophs and the related terrestrial and aquatic ecosystems represent carbon sinks for atmospheric CO_2 capture and fixation; whereas at downstream stages, emerging technologies to enable carbon utilisation and waste-sourced biorenewables have potentials to catalyse a low-carbon and resource circular bioeconomy. The biorenewable system complexity spans from resource-environment interaction underpinned by photosynthesis and biogeochemical cycles to the interlinked subsystems across upstream ecosystems and downstream manufacturing. Upstream resources e.g. terrestrial and aquatic plant species are regulated by environmental drivers whereas their availabilities are constrained by capacities and boundaries of natural and built capital assets; thereby, the downstream technology solutions may vary at different spatial and temporal scales due to the variability in resource quality and quantity. Unlocking complex resource-biorenewable-waste systems is mandatory to catalyse a sustainable circular bio-economy transition. By reviewing the state-of-the-art computational methods, this study presents a whole systems approach where spatial data analyses, advanced statistical methods, first principle models, quantitative evaluation of sustainability and mathematical optimisation are coupled and integrated into a multi-scale modelling framework. This framework inherently links the processes and subsystems across ecosystems and biorenewable manufacturing. Reflecting the fundamental computational methods and modelling advances, our study provides insights into the emerging opportunities and highlights the identified frontier research directions to unlock the complexity of biorenewable systems.

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