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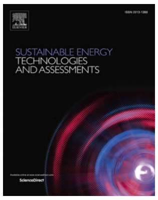

Review article

Biofuel production from Nature’s sugars: New horizons in the carbohydrate economy

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ABSTRACT

The carbohydrate economy harnesses the natural ability of photosynthetic organisms to convert atmospheric CO_2 into carbohydrates, offering significant advantages for integration into existing agricultural and industrial infrastructures. By selecting carbohydrate-producing systems that align with local economic contexts, it is possible to create robust value chains and ensure equitable benefit distribution. Furthermore, carbohydrate-derived biofuels can be seamlessly incorporated into current fuel infrastructures, eliminating the need for extensive technological overhauls. This review examines recent advancements in carbohydrate production factories and emerging technologies for converting carbohydrates into biofuels. These innovations represent a promising bridging strategy in the transition toward low-carbon solutions, with the potential to significantly reduce reliance on fossil carbon resources and promote more equitable energy and income distribution. Such progress can help foster a society better equipped to address the interconnected challenges of climate change, resource depletion, and growing energy demands.

1. Introduction

We live in an era of profound changes. And this requires the implementation of appropriate strategies for our progress. As stated in Bertrand Russell’s Unpopular Essays [1], a stark difference exists between the two terms. “Change” is scientific, while “progress” is ethical; change is undeniable, whereas progress is debatable. Human race will have change, whether like it or not. However, real progress can only be made when designing rules that direct human and economic resources toward the creation of a society and economy based on both human needs and human nature [2]. The carbohydrate economy (CE) aligns with this direction.

Around 200 years ago, industrialized societies were CEs. Plants were the primary raw material in the production of dyes, chemicals, paints, inks, solvents, construction materials, and energy. For instance, from January 1807, the city of London was progressively illuminated by gas-fueled lamps, as a more reliable and cost-effective solution compared to candles or oil lamps. This gas was obtained through gasification of wood coal. By 1860, gas lighting was to be found in most all over Britain and in most European cities. In the same year, corn-derived ethanol was a best-selling industrial chemical, and as late as 1870, wood provided 70% of the U.S. energy. Two tons of vegetable biomass for every one ton of minerals were used [3]. Cotton and wood pulp provided many widespread materials, such as nitrocellulose, cellophane, Rayon fiber, and acetate yarn.

However, a tumultuous change was imminent. The Industrial Revolution, which began with stationary wind- and water-powered technologies, rapidly shifted to an almost complete reliance on fossil hydrocarbons: coal in the 19th century, oil in the 20th Century, and subsequently, natural gas. Humanity’s dependence on fossil hydrocarbons for energy increased nearly 800-fold since 1750 [4]. Within just 25 years, the carbohydrate-based economy virtually disappeared, undermined by the remarkably low prices of crude oil and the rapid emergence of a diverse array of inexpensive products derived from it. The unprecedented — and likely unrepeatable — availability of high-density fuels, coupled with advances in refining, triggered an extraordinary

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acceleration in human development and population growth, rising from 0.8 billion globally in 1760 to over 8.1 billion in 2024 [5]. This surge was significantly supported by the advent of fossil-derived ammonia, which enabled the large-scale production of cost-effective and efficient fertilizers. The strong correlation between per capita energy consumption and the UN's Human Development Index further highlights this connection [6]. While this energy shift brought substantial socio-economic improvements, particularly in the Global North, it also triggered widespread social turbulence [7] and profound political transformations [8]. The emergence of localized, high-income opportunities associated with fossil resources prompted global dominant actors to compete for control, exacerbating inequality. According to UNESCO's 2022 World Inequality Report [9], global inequality rose sharply between 1820 and 1910 before stabilizing at persistently high levels. A key driver of this inequality was Europe's colonial expansion, which peaked between 1910 and 1950.

Following World War II, colonial control by imperial nations weakened; however, significant economic and political power increasingly became concentrated among financial elites, who exploit global markets to amass substantial portions of global wealth. In 2022, the bottom 50% of the global population held only 2% of total wealth, while the top 10% controlled a staggering 76% — an extreme imbalance projected to worsen [9]. The entrenched economic advantages of dominant actors, combined with their ongoing economic and political interference in newly decolonized nations, have prevented many countries from realizing true socio-economic benefits from their own resources, particularly in the Middle East [10] and North Africa.

Unfortunately, income equality — rather than "uncontrolled economic growth" — is a fundamental "beneficial provisioning factor" for fostering virtuous socio-economic conditions [11]. Other crucial factors for achieving this goal include access to clean energy (UN Sustainable Development Goal 7) and the quality of public services.

The fossil energy revolution has also been closely linked to rising atmospheric greenhouse gases (GHGs), primarily CO_2, resulting from fossil fuel use and deforestation. This increase has driven global warming and brought about a range of environmental, ecological, and socio-economic challenges. Reducing atmospheric CO_2 has therefore become a cornerstone of sustainable development and a critical strategy for mitigating human impacts on the planet. The UN Climate Change Conference has highlighted the urgent need for a low-carbon energy transition based on three key pillars: (i) expanding renewable energy to replace fossil fuels; (ii) improving energy efficiency across industrial, residential, and transportation sectors; and (iii) developing advanced energy storage technologies to manage the intermittency of renewables. While these pillars provide clear pathways, the strategies required to achieve them remain highly contentious.

Maintaining economic stability within a carbon-based economy while drastically cutting CO_2 emissions presents significant challenges, particularly for nations where the transition to fossil energy is still unfolding. Therefore, the ideological pursuit of these measures risks further exacerbating global inequalities. The dominant international perspective, rooted in ecological modernization theory [12], assumes that technological progress, improved energy efficiency, and a gradual shift to renewable energy — alongside carbon capture, utilization, and storage (CCUS) — can deliver a sustainable energy transition within existing political and economic systems. However, there is no empirical evidence to support the rapid and absolute decoupling of GHG emissions from economic activity that this vision requires [13]. Indeed, recent shifts among leading global asset managers, who are moderating their commitments to decarbonization [14], reveal how financial power and political considerations continue to shape these strategies. Finally, the Intergovernmental Panel on Climate Change underscores the need for profound societal transformations, including changes in social structures, political systems, and power dynamics, to achieve a climate-resilient and sustainable future [15].

Humanity is now navigating through another period of profound change, in which increasing energy demands must contend with the progressive depletion of fossil resources [16]. Addressing this urgent challenge requires immediate and decisive action to establish a sustainable path forward. However, the intricate interplay of economic, environmental, and geopolitical dynamics has given rise to diverse visions for progress. Among these, a pragmatic alternative to the "carbophobic" perspective — which views CO_2 solely as a pollutant to be eliminated — is to recognize CO_2 as a renewable carbon resource. In particular, leveraging the inherent capacity of photosynthetic organisms offers an efficient and sustainable strategy for enabling a carbon-based economy, which remains fundamental to industrial activity and global development. These organisms naturally convert atmospheric CO_2 into reduced biomolecules such as polymeric carbohydrates and lignin, simply by exploiting solar energy — in contrast to the complexity and high costs associated with CO_2 CCUS.

Efficiently transforming these biopolymers into biofuels is a crucial step toward establishing a sustainable, carbon-based energy strategy. This strategy, collectively defined as the CE, should prioritize minimizing agricultural land use, preventing competition with food and feed production, establishing local value chains, and promoting the equitable distribution of benefits. Biofuels produced within the CE — derived from C5/C6 sugar platform biorefineries — not only have reached significant maturity but also offer a seamless transition to sustainable energy by integrating with existing fuel infrastructures. Their compatibility with conventional fuels allows the continued use of established technologies in critical sectors such as transportation and industry, including internal combustion engines (ICEs). Ongoing research aimed at improving ICE efficiency [17] could further enhance the viability of carbohydrate-based biofuels.

These developments position the CE as a promising transitional technology, capable of meeting future energy and carbon material demands while supporting the shift toward advanced low-carbon solutions such as wind, solar, hydropower, and green hydrogen. Moreover, as will be explained later, further synergies exist between the CE and emerging low-carbon technologies. For instance, the CE can integrate effectively with the green hydrogen economy and with direct CO_2 electroreduction (CO_2ER) technologies, both of which are essential for developing e-fuel infrastructures.

This review highlights both current strategies and emerging approaches that promise greater sustainability in carbohydrate fractions production (Section 2) and their conversion into biofuels (Section 3). While the production of vegetable-derived lipids, such as triglycerides, may also contribute to the CE, this report excludes them due to their organism specificity, reliance on agricultural land, and associated scale limitations. Advances in carbohydrate biomass production and conversion into biofuels align with circular economy principles, transforming waste materials into valuable energy re-sources. These innovations promise to accelerate the global energy transition while addressing environmental and economic challenges.

2. Sources of biobased carbohydrates

Biobased carbohydrates can be sourced from various biorefineries, which are classified according to the type of biomass feedstock used.

2.1. *First generation biorefineries*

First-generation biorefineries (1st-BRs) are designed to utilize easy-to-fractionate feedstocks containing sugars in monomeric or oligomeric forms. These feedstocks often require minimal processing, such as mechanical extraction, to produce sugar solutions, whereas starch-based feedstocks need additional, relatively simple hydrolysis steps. In 1st-BRs, these monosaccharides or disaccharides solutions are predominantly converted into bioethanol through the well-established alcoholic fermentation by yeasts [18].

Sugarcane (*Saccharum* spp.), comprising 10–15% soluble sugars (primarily sucrose, glucose, and fructose) and 10–16% fiber (cellulose, hemicellulose, and lignin), is a highly convenient feedstock. Its sugars can be directly fermented by yeasts, making the process energy-efficient [18–20]. Sugarcane's productivity (6,470 L_{EtOH}/ha) surpasses that of sugar beet (5,500 L_{EtOH}/ha) and corn (4,180 L_{EtOH}/ha) [18,21,22]. The production process involves crushing the stalks to extract juice for fermentation, while the fibrous residue (bagasse) is burned to generate heat and electricity, improving the process energy balance [22]. On a life-cycle basis, sugarcane ethanol reduces GHG emissions by 84%, outperforming sugar beet ethanol (40%) and corn ethanol (30%) [23]. Global sugarcane production has increased significantly since the year 2000, reaching 2.03 billion tons in 2023, with approximately 39% produced in Brazil and about 25% in India [24].

Corn (*Zea mays*) kernels contain approximately 72% of starch [25], composed of D-glucose units, bonded in two forms: amylose, which is water-insoluble and relatively resistant to hydrolysis; and amylopectin, which is more easily hydrolyzed. The cheapest corn-to-ethanol process involves the dry grinding of the kernels to produce corn flour [26], which is then suspended in water and hydrolyzed to oligomeric dextrins [26–29], later subjected to simultaneous saccharification and fermentation to a 14–20 vol% water solution of ethanol [27,30]. Once ethanol is recovered through distillation, the remaining slurry (whole stillage) is centrifuged to give a liquid fraction (thin stillage) which is recycled, and a solid fraction (distiller's dried grains with solubles, DDGS) which find application as animal feed [26]. Corn oil is another useful co-product. The dry grinding process, accounting for 92% of U.S. production, yields ~ 11 L of ethanol, 6.7 kg of DDGS, and 0.4 kg of corn oil per bushel (~25 kg) of corn grains, along with 7.2 kg of CO_2 [31]. In the alternative wet-milling process, corn is fractionated into starch, germ, fiber, and solubles, with starch processed for ethanol and coproducts such as germ meal, corn gluten feed, and corn oil. While costlier, this method produces higher-value coproducts [25]. Global corn production reached 1.24 billion tons in 2023, with approximately 32% produced in US and about 23% in China [32].

With a yield of ~ 3,740 L_{EtOH}/ha [31,33], **wheat** (*Triticum aestivum*) is less productive than sugarcane or corn, due to its higher protein content [34]. A critical limitation derives from its role as a staple food crop, thus evidencing concerns over food security.

The large-scale implementation of 1st-BRs has driven a significant expansion in global bioethanol production, making it the most widely produced biofuel [35–38]. Over the past 15 years, production has grown from 66.6 billion liters in 2008 to 111.7 billion liters in 2023 [31]. The U.S., accounting for 52.5% of global production, primarily uses corn as a feedstock, while Brazil, responsible for 28.0% of global production, predominantly relies on sugarcane [31,33,38–41]. Corn-based ethanol in the U.S. faces challenges due to competition with soybean production, which limits its scalability [22,42]. In contrast, Brazil's sugarcane ethanol has thrived, becoming a cornerstone of the country's renewable energy strategy [43,44]. This strategy is focused on creating an irreversible shift away from fossil fuels [45] by leveraging "precision agriculture" and other advanced technologies to enhance farm efficiency [46–49]. These efforts position Brazil's sugarcane industry as a global leader in sustainable bioethanol production.

First-generation feedstocks have played a central role in the initial development of biofuel production. However, two major challenges limit their sustainability and long-term viability:

I. Food vs. fuel dilemma: 1st-BRs present a significant challenge as their feedstocks compete directly with food and feed supplies, creating tension between energy security and food security [50]. Staple crops like rice, wheat, maize, and cassava form a vital part of the diet for many populations, providing essential sugars, micronutrients, and vitamins. The increasing use of corn for bioethanol production has driven up animal feed prices, affecting the entire livestock sector [51]. This trend exacerbates food shortages, especially in developing countries where a significant portion of household income is spent on food. Consequently, rising food prices can deepen food insecurity and potentially trigger social unrest [31,50–54]. Additionally, higher feed costs ripple through food supply chains, increasing the prices of meat, dairy, and other animal-based products [19].

II. Carbon cycle benefits and limitations: Although biomass growth contributes to CO_2 fixation, achieving true carbon neutrality is complex due to the energy demands and inefficiencies of each stage of production [55–57]. Life cycle assessment (LCA) studies highlight the environmental impact of agricultural practices, including the use of fuel-powered machinery for planting, harvesting, and transportation. Furthermore, fertilizers release nitrous oxide, a potent GHG, during farming [58,59]. Addressing these issues requires improved agricultural practices to enhance the sustainability of bioethanol production [60]. Using marginal lands unsuitable for food crop cultivation offers a promising solution to reduce pressure on food supply chains [61,62]. Similarly, utilizing renewable energy sources, such as biomass or biogas, in sugar-to-biofuel processes significantly lowers CO_2 emissions compared to coal-powered machinery [63,64]. According to the U.S. Environmental Protection Agency, corn-based bioethanol reduces GHG emissions by 39–43% compared to gasoline [65]. However, the sustainability debate surrounding 1st-BRs extends beyond GHG emissions, necessitating evaluations of water use, soil degradation, biodiversity loss, and air pollution.

2.2. Second generation biorefineries

Second-generation biorefineries (2nd-BRs) offer a significant leap in sustainability compared to their first-generation counterparts by utilizing lignocellulosic (LC) biomass. Typical feedstocks include agricultural residues like corn stover and wheat straw, forestry residues, and dedicated non-food energy crops such as switchgrass or miscanthus. Similar to 1st-BRs, 2nd-BRs rely on arable land and conventional farming practices [66,67]. LC biomass primarily comprises three biopolymers [67]: (i) cellulose (35–50%), a linear polymer of D-glucose [68]; (ii) hemicellulose (20–35%), a branched polymer containing pentoses (xylose, rhamnose, and arabinose), hexoses (glucose, mannose, and galactose), and uronic acids [69]; and (iii) lignin (15–30%), a cross-linked polymer composed of three phenolic monomers [70–72].

While 2nd-BRs address the food vs. fuel dilemma by utilizing non-food LC feedstocks, processing these materials is more challenging due to their complex structure. The presence of lignin and the crystalline form of cellulose reduce reagent accessibility, diminishing process efficiency [69,73–75]. Releasing usable sugars from LC biomass requires advanced processing techniques, typically involving two stages:

I. Pretreatment [76] is a critical step in improving reagent accessibility while minimizing the generation of inhibitory compounds (e.g., furfural, hydroxymethyl furfural, acetic acid, phenolics) that can hamper downstream fermentation [77–79]. Pretreatment methods are classified into four categories.

Ia. Physical. Grinding, irradiation, or pulsed electric fields.

Ib. Chemical. Using agents like acids, bases, ozone, organic solvents, ionic liquids, or deep eutectic.

solvents [80].

Ic. Physicochemical. Combining physical and chemical methods, such as CO_2 explosion, liquid hot water treatment, autohydrolysis, or ammonia fiber explosion [81,82].

Id. Biological. Utilizing microorganisms for delignification [83,84].

II. Hydrolysis. Involves the conversion of carbohydrate fractions into monomeric or oligomeric sugars. Developing cost-effective hydrolysis methods is essential for sustainable 2nd-BR operations. Strategies to improve efficiency include: (i) incorporating surfactants, plant-derived proteins, and bio-based additives to enable low-enzyme-load hydrolysis [85–87], and (ii) using thermotolerant lignin-degrading fungal strains to enhance the hydrolysis [88,89]. These also helps to avoid excessive dilution, which brings to costly post-processing concentration steps [90–92].

Traditional carbohydrate-focused 2nd-BRs employ pretreatment methods primarily focused on physically removing lignin from the sugar biopolymers [71,93], alike in the sulphite pulping process [94–98]. However, this brought to the alteration of the lignin's structure towards a more intractable (recalcitrant) form [69,99], relegating lignin to a by-product burned to obtain process energy.

An improved "lignin-first" approach, also known as reductive catalytic fractionation (RCF) has emerged in recent years, achieving effective fractionation of LC biomass into lignin-rich oil and carbohydrate-rich pulp (Fig. 1) [100–105].

RCF operates at high temperatures (180–260 °C), moderate pressures (20–120 bar), and in presence of organic solvents (e.g., alcohols, glycols), hydrogenation catalysts (e.g. Pd/C [106–111], Ru/C [102,107,112–114], or Ni-Al_2O_3 [102,104,115–118]), and H_2 (or a hydrogen donor solvent [100]).

Differently from carbohydrate-focused approaches, RCF produces high-quality lignin-rich oil, suitable for various downstream processing towards phenols [119], bisphenols [120], catechol [121], propylene [104], aromatic amines [122,123], and biofuels [124,125]. Additionally, the higher molecular weight fraction of the lignin oil, composed of dimeric and oligomeric polyols, find application for producing polyurethanes [125], epoxy resins [126–130], temperature-resistant lubricants [131], and varnishes or inks [104].

In some RCF-based biorefineries, an overemphasis on the lignin fraction can negatively impact the carbohydrate/pulp component, leading to significant losses during lignin oil refining [100,103,132]. However, recent innovations, such as atmospheric-pressure RCF [93], and alkali-assisted solvent methods [71], have demonstrated improved yields and delignification rates. Another RCF process has proved to achieve 50% delignification while retaining 82% of C6 sugars and 73% of C5 sugars in the pulp [100].

2.3. *Third generation biorefineries*

Third-generation biorefineries (3rd-BRs) utilize non-traditional biomass sources, such as microalgae and seaweed, offering distinct advantages over 1st-BRs and 2nd-BRs. These include:

- Avoidance of food competition, thanks to the use of non-food feedstocks, bypassing the food vs. fuel dilemma.
- High productivity, as algal biomass exhibits rapid growth and enhanced CO_2 biofixation rates per unit area compared to terrestrial plants.
- Reduced land-use involvement, as algae can be cultivated on non-arable land.
- Simplified processing, as algal biomass lacks lignin, easing conversion processes compared to LC biomass [133,134].
- More controlled cultivation through the use of photobioreactors, enabling steady biomass production, that is independent of seasonal constraints.
- Wastewater treatment integration, through the mixotrophic growth algae cultivation, where algae can use waste organic substances as carbon source [135].
- Lower resource demands, due to the necessity of fewer fertilizers, pesticides, and freshwater compared to terrestrial crops [136,137].

Despite their potential, 3rd-BRs also face some challenges, such as:

- high initial capital costs for plant setup;
- energy-intensive harvesting and processing;
- limited technological maturity and cost-effectiveness at an industrial scale.

Seaweed cultivation is a fast-growing activity, with a global production that reached 35.1 million tons in 2022, largely occurring in Asia, particularly in China and Indonesia [138,139]. Brown (e.g., *Laminaria japonica*, *Saccharina latissima*, *Padina tetrastromatica*), red (*Gelidium amansii*, *Ahnfeltia plicata*) and green (*Codium fragile*, *Ulva lactuca*) marine seaweeds constitute relevant sugar sources [140]. Acid hydrolysis and/or enzymatic saccharification [141–144] are the standard techniques adopted to obtain monomeric and oligomeric sugars fractions from these, while other specialized methods such as ultrasonication [145,146] and/or pulsed electric field processing proved to enhance carbohydrate extraction and improve downstream processing, reducing toxic elements in the biomass extract [147,148].

Microalgae, comprising approximately 50,000 known species, thrive in both freshwater and saltwater environments [149]. These organisms efficiently convert CO_2 into intracellular metabolites, such as starch, lipids, and proteins [150]. Their productivity and biomass composition

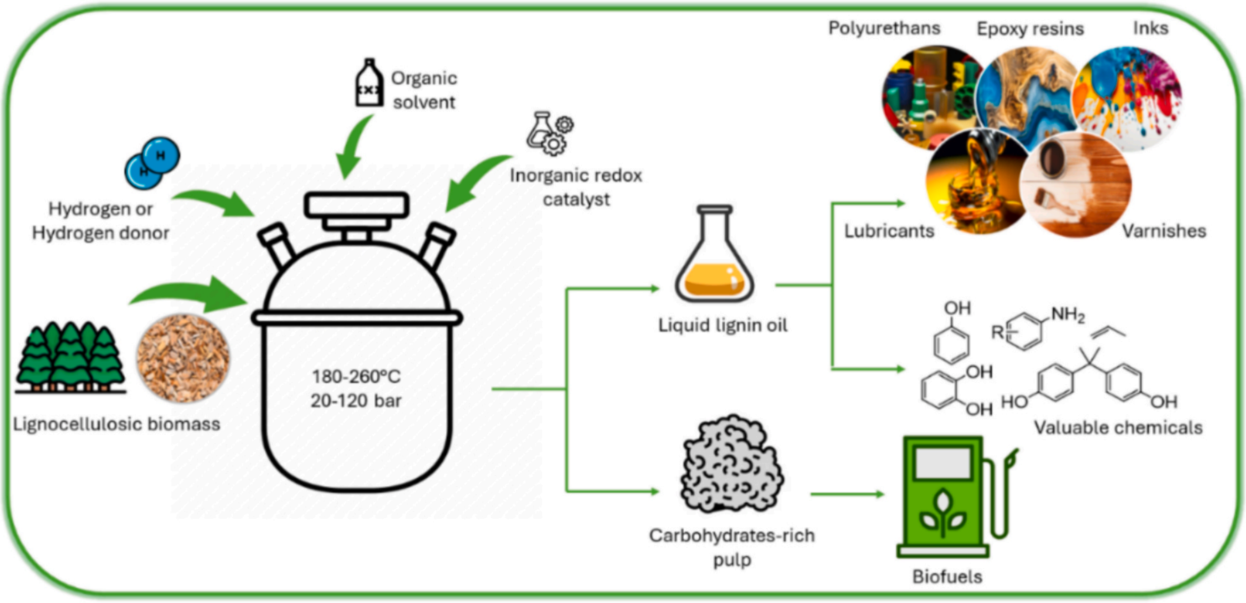

Fig. 1. Schematic representation of a RCF process.

depend on factors like: specific strain [151], harvesting time [152], light availability [153], CO_2 and O_2 levels [154], and cultivation temperature [155,156]. Essential macro- (N, P, S) and micronutrients (K, Fe, Mg, Ca) are also important to support structural development [157].

Aside from these general characteristics, each organism has a natural tendency to accumulate specific biopolymers based on its predominant metabolic pathways. However, various techniques can be used to induce metabolic shifts, leading to the accumulation of biomolecules that are typically produced in only minor amounts. These techniques include specific cultivation practices [158], genetic modifications [159], nutrient adjustments [160], the addition of exogenous phytohormones [161–165], and the application of environmental stress [166–169]. Among these, externally controllable environmental stresses — such as nitrogen starvation and carbon abundance [170] — are the most commonly employed methods for enhancing carbohydrate accumulation in microalgae.

Among microalgae, cyanobacteria (*Spirulina*) and chlorophytes (*Chlorella*) are extensively studied for their versatility and robustness [171–173]. Their high protein content (63% and 58% of dry mass, respectively) makes them valuable for food and feed applications [174]. However, carbohydrate accumulation in these species can be enhanced by: nitrogen deprivation [175], high CO_2 concentration [176–178], mixotrophic cultivation using organic-rich wastewaters [179,180], increased light intensity [160], or osmotic stress from high salinity [133].

2.4. Higher generation biorefineries

Research into advanced photosynthetic systems, hybrid bioelectrochemical systems, and semi-artificial or artificial biological systems represents a natural progression of 3rd-BRs [181–183]. Notably, recent literature reports the development of artificial chemical–biochemical hybrid photosynthetic systems capable of synthesizing starch [184] or sugars [185] directly from CO_2.

The use of engineered enzymes and genetically modified microbes is an emerging frontier in biorefinery research. Genetic modification can be employed to improve photosynthetic efficiency, and boost carbon fixation pathways [186]. C1-assimilating microorganisms, which can biosynthesize value-added compounds such as carbohydrates, show significant promise despite current limitations in carbon fixation efficiency at scale [187]. Several processes utilizing heterotrophic microorganisms like *Escherichia coli* and yeasts (*Pichia pastoris*, *Saccharomyces cerevisiae*, and *Ogataea polymorpha*) have demonstrated the production of diverse biofuels and fine chemicals from C1 carbon sources [181].

Electro-biochemical systems, which integrate electrochemical and biological processes to enable novel carbon fixation strategies, have advanced significantly in recent years. One approach involves the direct attachment of microorganisms to electrodes, enhancing electron transfer for *ex situ* carbon fixation [188]. Alternatively, spatially decoupled systems generate intermediates — such as CO, syngas, or formate [189] — via electrocatalysis, which are then fed into separate bioreactors where microorganisms convert them into high-value compounds [188,190]. A notable innovation is a hybrid electro-biosystem combining CO_2ER to acetate with yeast fermentation, achieving highly efficient glucose production [191]. These advancements demonstrate the seamless integration of bioconversion pathways with CO_2ER technologies, which can produce reduced C1 carbon compounds (e.g., CO, formic acid, methanol, methane) and even C2+ compounds from CO_2, using (renewable) electrical energy [192].

Artificial photosynthesis (AP) aims to replicate natural photosynthesis by converting and storing solar energy in chemical bonds. While AP systems have garnered significant attention, they still face challenges related to efficiency and stability, requiring further refinements for practical implementation [193]. Bottom-up assembly of synthetic biochemical components opens new opportunities for artificial systems. Inspired by the compartmentalized architecture of cells and organelles, lipid and polymer vesicles are being developed as versatile model membrane systems. These vesicles provide precisely tailored environments for synthetic biological processes, enabling applications that were previously unattainable [194].

3. Conversion of carbohydrates into biofuels

Several distinct methods are available to convert carbohydrates into biofuels, each with its own advantages and technological challenges.

3.1. Chemoconversion of carbohydrates

Chemoconversion involves the transformation of carbohydrates through chemical processes. This approach exploits advancements in artificial catalysts and optimized reaction conditions to achieve high selectivity and lower energy expenditure compared to typical thermochemical processing (Section 3.2) [195]. Additionally, chemoconversion processes are simpler to implement and scale up than bioconversion methods (Section 3.3).

Four key unit operations are commonly applied to chemically upgrade carbohydrates, as follows:

I. Acid-catalyzed dehydration (ACD) [196], where acidic catalysis at low-to-moderate temperatures efficiently removes oxygen from monomeric or oligomeric sugars. This energy-efficient process exploits the formation of stable five-membered furanic structures. In certain cases, acid-catalyzed isomerization (e.g., glucose to fructose or xylose to xylulose) can occur within the same reaction vessel, streamlining the process and reducing operational complexity.
II. Catalytic hydrolysis (CH) [197], devoted to the selective depolymerization of polysaccharides, often with simultaneous upgrading into furanics, polyols, or other added-value compounds. These processes, which are akin to mild thermochemical methods, typically operate within a temperature range of 170–200 °C under acid catalysis.
III. Hydrodeoxygenation (HDO) [198], which utilizes hydrogen and a metal catalyst at moderate temperatures to reduce oxygen content in carbohydrates or their derivatives. This process can occur in the aqueous phase, depending on the substrate and operating conditions. Further details on HDO are provided in Section 3.2 due to its similarities with thermochemical methods.
IV. C-C coupling, involving the formation of new carbon–carbon bonds, often via aldol-type reactions [199]. This enables the production of compounds with carbon backbones longer than five or six atoms, thereby broadening the scope of biofuels and chemicals derived from carbohydrate feedstocks.

The sequence and combination of the described unit operations in real processes depends on the carbohydrate source and define the main selectivity of the overall process. In the following, the main carbohydrate chemoconversion processes are reported, with a classification based on the key platform chemical (PC) involved.

Furfural (FA) is a well-known PC, with significant potential in materials chemistry and in the energy sector. It is primarily produced from the hemicellulose fraction of LC biomass, with current global production of ~ 4.2 million tons per year. A techno-economic evaluation demonstrated that FA can be efficiently produced using a lignin-first approach (detailed in Section 2.2). This approach involves processing prehydrolysates from kraft hardwood dissolving pulp mills via membrane filtration and dehydration [200]. FA production is based on ACD, which first promote the isomerization of xylose to xylulose, and is followed by the removal of three water molecules (Fig. 2) [201], achieving substantial oxygen removal with complete retention of carbon atoms.

FA can be reduced catalytically to furfuryl alcohol (FAL), a key monomer for furanic resins. FAL also serves as a critical intermediate for

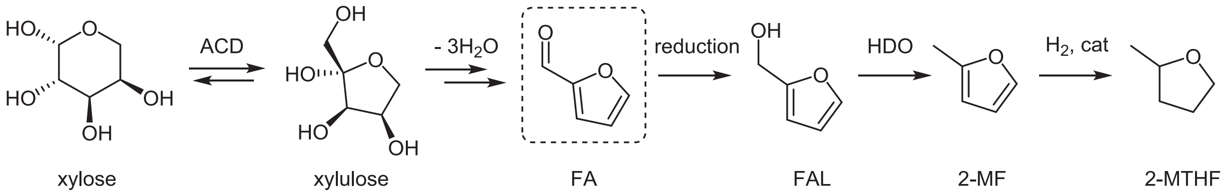

Fig. 2. Chemoconversion of xylose into FA, and follow-up upgrading.

biofuel and fuel additive production. For instance, HDO of either FAL or FA produces 2-methylfuran (2-MF), a potential drop-in biofuel for gasoline [202]. However, the inherent toxicity of 2-MF restricts its large-scale application. To overcome this limitation, further hydrogenation of 2-MF yields 2-methyltetrahydrofuran (2-MTHF), a liquid fuel with broader usability and applications as a biobased solvent for the chemical industry [203].

5-Hydroxymethylfurfural (5-HMF), a well-established PC, is obtained through the chemical upgrading of C6 sugars, such as glucose or fructose, with complete retention of carbon atoms. The mechanism, while complex and partially debated, involves an ACD which includes a first glucose-to-fructose isomerization, followed by a triple dehydration step (Fig. 3) [204].

Efficient conversion of monomeric sugars to 5-HMF has been established [205]. However, the direct conversion of cellulose to 5-HMF still suffers from low yields and selectivity [206], reflecting the challenges inherent in processing more complex feedstocks. Selected cellulose sources with enhanced hydrolyzability, such as microalgae, show promise for improving outcomes [207]. 5-HMF can be reduced to 2,5-bis(hydroxymethyl)furan (BHMF), a valuable diol with applications in polymer chemistry and a key intermediate for producing, via HDO, 2,5-dimethylfuran (2,5-DMF). This compound is a promising drop-in biofuel for gasoline, featuring 40% higher energy density, higher boiling point (92 °C), greater hydrocarbon solubility, and lower water adsorption compared to ethanol [202]. Further hydrogenation of 2,5-DMF affords 2,5-dimethyltetrahydrofuran (2,5-DMT), a fuel oxygenate and a less polar, higher boiling point solvent, compared to tetrahydrofuran [208]. Moreover, oxidation of 5-HMF, affords 2,5-furanedicarboxylic acid (FDCA), which gained considerable attention as a bio-based alternative to terephthalic acid, *i.e.* as a monomer for plastics. The oxidation can be also stopped at the dialdehyde 2,5-diformylfuran (DFF).

The simultaneous production of FA and 5-HMF from biomass represents an interesting strategy for the sustainable production of biofuels. HDO of both FA and 5-HMF produces a mixture of 2-MTHF and 2,5-DMT, which is suitable as gasoline-range fuels [209,210]. Research on ACD catalysis is a fundamental field of innovation. Zeolites, for instance, have emerged as robust catalysts for producing FA and 5-HMF due to their chemical resistance, acidic properties, and thermal stability [211,212]. Adsorbing Brønsted acids onto silica provides an alternative approach to achieving heterogeneous acid catalysis, replicating the functionality of homogeneous systems while simplifying catalyst recovery [213,214]. Alternatively, metal–organic frameworks were also evaluated as solid catalysts [215,216]. Electrochemical transformations of FA and 5-HMF provide an environmentally friendly alternative to traditional oxidation and reduction processes. For instance, electrocatalytic hydrogenation of FA can afford 2-MTHF [217], while electroreduction of 5-HMF gives access to BHMF [218]. On the other hand, electro-oxidation of 5-HMF can produce DFF or FDCA.

Levoglucosan (LGA), **levoglucosenone** (LGO), and 5-HMF, are the main products of CH, (also known as catalytic depolymerization [219]) of cellulose (Fig. 4) [220]. Among these, LGO is a particularly versatile PC.

Mild hydrogenation of LGO, for example, gives access to cyrene, a DMF-like solvent with great potential [221], while stronger hydrogenation affords useful biobased diols.

Isosorbide is another valuable PC [222], showing straightforward pathways to biofuel production [223]. It is commonly obtained from sorbitol, the hydrogenation product of glucose (Fig. 5), but it is also directly obtainable from cellulose [224].

Levulinic acid (LA), an acidolysis product of 5-HMF [225], is another crucial PC (Figs. 4 and 6). LA is readily produced from fructose or cellulose, resulting in the loss of one carbon atom as formic acid. Its production from biomass hydrolysis can occur simultaneously with 5-HMF generation, enabling a dual-product system that enhances overall process sustainability [225,226].

LA can also be obtained through the hydrolysis of FAL with complete retention of carbon atoms, while alcoholysis of FAL yields levulinic acid esters (LAEs). This indicates an alternative route to obtain the direct conversion of C5 carbohydrate-rich biomass into LA or LAEs, with intermediacy of FA. Suitable feedstocks for LA production include macro- [227] and micro-algae as well [228]. The presence of both carbonyl and carboxyl functional groups in LA offers extensive opportunities for chemical upgrading, establishing LA as a versatile precursor to numerous value-added products [226]. In the fuel sector, LAEs stand out as promising oxygenate additives for gasoline and diesel, showing a range of applications depending on the alkyl chain length. Ethyl levulinate, for instance, can be used as a diesel miscible biofuel [229], while hexyl levulinate is reported to improve the fuels' cold flow properties, decrease NO_x emissions, and stabilize the flash point [226]. Advancements in heterogeneous catalysis have improved LAEs production [189,230], offering operational and environmental benefits over traditional mineral acids. Zn$^{(II)}$-catalyzed double esterification of LA with

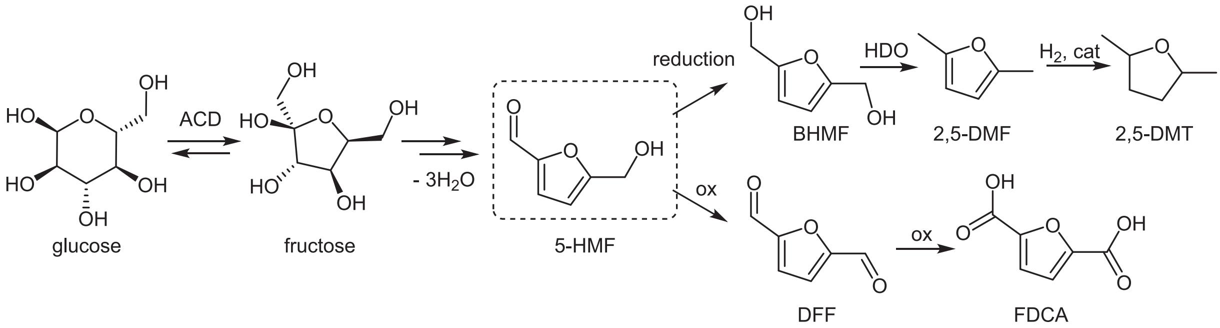

Fig. 3. Chemoconversion of glucose into 5-HMF, and follow-up upgrading.

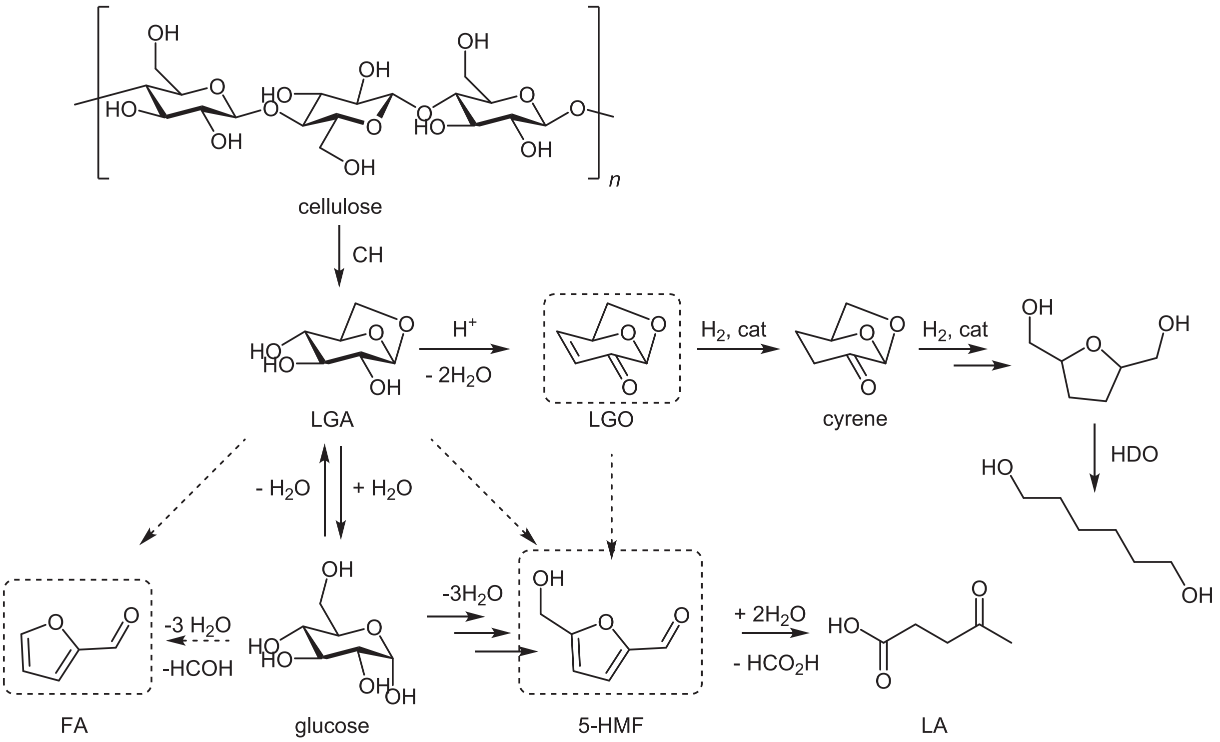

Fig. 4. CH of cellulose into LGA and LGO, and follow-up upgrading.

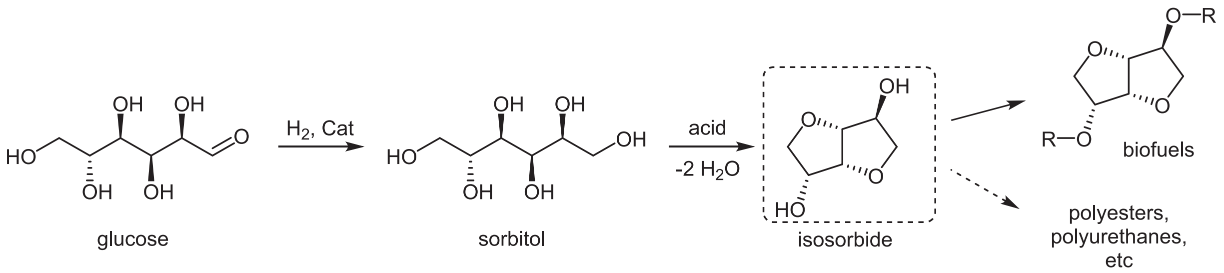

Fig. 5. Chemoconversion of glucose into isosorbide and following upgrading.

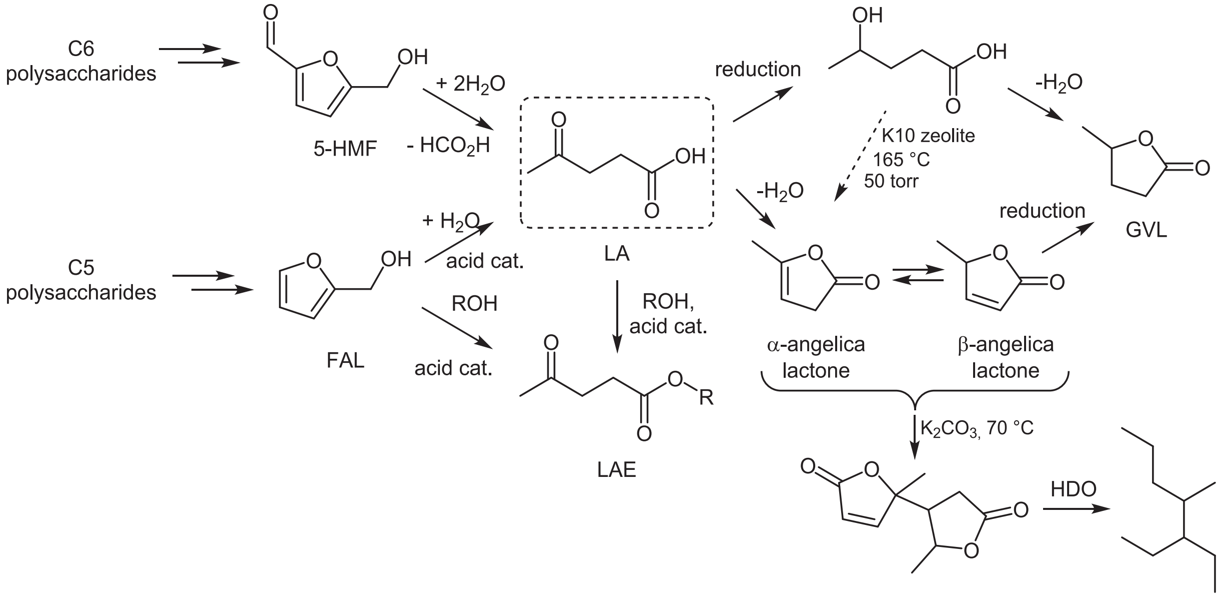

Fig. 6. Chemoconversion of C5/C6 carbohydrates into LA, and follow-up upgrading.

diols have broadened the range of possible fuel products [230].

***γ*-Valerolactone** (GVL), obtained through selective reduction of LA [231] or derived from FA [232], is a highly versatile compound with significant applications as both a green solvent and a fuel additive. The marked reactivity of angelica lactone, particularly regarding its alkaline dimerization (Fig. 6), offers a good option for the production of branched C7–C10 gasoline-like hydrocarbons through HDO [233].

Except the peculiar attitude evidenced by angelica lactones, a notable limitation of all the previously described approaches is the intrinsic limitation to short carbon-chain (five or six carbons) products, restricting their applicability to lighter biofuels. To overcome this limitation, new C-C bonds can be formed through aldol processes, exploiting the reactivity of already present carbonyl groups (e.g. in FA, 5-HMF, and LA), or of those obtained from the oxidation of primary hydroxylic functions. Coupling aldol condensation processes with subsequent hydrogenation enables the production of fuels across a wide spectrum, from lighter gasoline [234] to heavier jet fuels [235] and intermediates suitable for diesel applications. For example, the coupling of a short-chain ketone with two FA units yields a jet fuel precursor [236]. Another example involves the oxidative coupling of FA with alcohols in alkaline media [237], without the need for any expensive transition metal catalysts. Using ethanol, a C7 fuel can be obtained, while the use of different alcohols, results in fuel precursors tailored to distinct fuel ranges. The base-catalyzed aldol condensation of LA and FA affords, after HDO, a C20 fuel precursor, which can be further processed without separation into smaller oxygenates and hydrocarbons, ranging from C8 to C18 [238].

Other approaches capable to exploit the electrophilic properties of the carbonyl group and elongate carbon chains have also been explored for FA, 5-HMF, and LA. For example, alkylation of the furan nucleus easily affords dimeric or trimeric structures, which can be subjected to reduction into fuels [239]. Pinacol [240] or electropinacol dimerization of FA and/or 5-HMF also yields useful adducts having high potential as jet fuels [241]. Similarly, acyloin-type condensation of 5-HMF towards bisfuranic polyols enable the further conversion, through HDO, into C12 oxygenated diesel fuels with high energy density, or into C12 linear alkanes [242].

The hydroxyl group of 5-HMF also offers additional opportunities for modification. Etherification produces 5-ethoxymethylfurfural (EMF), a C8 precursor that, upon HDO, yields a gasoline-like fuel [243].

β-Diketones, β-ketoesters, and malonates [244] are useful compounds for biofuel production, particularly when derived from biomass. These compounds can undergo Knoevenagel condensation with carbonyl-containing substrates, facilitating the synthesis of elongated carbon chains. For instance, the reaction between acetylacetone and FA forms a high-quality fuel precursor which, upon HDO, affords a C10 alkane fuel with complete carbon atom retention [245]. Notably, the García-González Reaction (GGR) [246], a Knoevenagel condensation involving the carbonyl groups of carbohydrates, produces intriguing derivatives that often undergo dehydration or etherification within the same reaction vessel. While the GGR on pentoses typically produces polyhydroxyalkylated furans, a significant application of the GGR involves glucose, which can yield bicyclic products under controlled conditions. Indeed, the Lewis acid-catalyzed enolization of the 1,3-diketone, followed by nucleophilic attack on the sugar's carbonyl group (Fig. 7) [247] gives rise to a Knoevenagel intermediate, which then undergoes dehydration to form a furan moiety. This last, due to the enhanced electrophilicity of the adjacent carbinol group, cyclizes to produce C-glycosylfurans.

Hydrogenation and HDO of the glucose-derived GGR product can produce C11 alkanes [195,248]. The GGR's versatility has been demonstrated with disaccharides [249], as well as tri- and tetraoses [250], showcasing its broad applicability for carbohydrate-derived biofuel precursors.

3.2. Thermochemical conversion of carbohydrates

Thermochemical conversion involves transforming carbon-based resources — such as coal, biomass, or other organic material — into products like fuels, chemicals, or other value-added materials. These processes rely on heat, pressure, and catalysts to disproportionate carbon into energy-dense products (e.g., hydrocarbons, methane, hydrogen, and char) and oxidized byproducts (e.g., carbon dioxide and water). While thermochemical methods often demand significant energy inputs, their versatility and broad applicability make them indispensable for converting diverse carbon feedstocks. Classical methods like

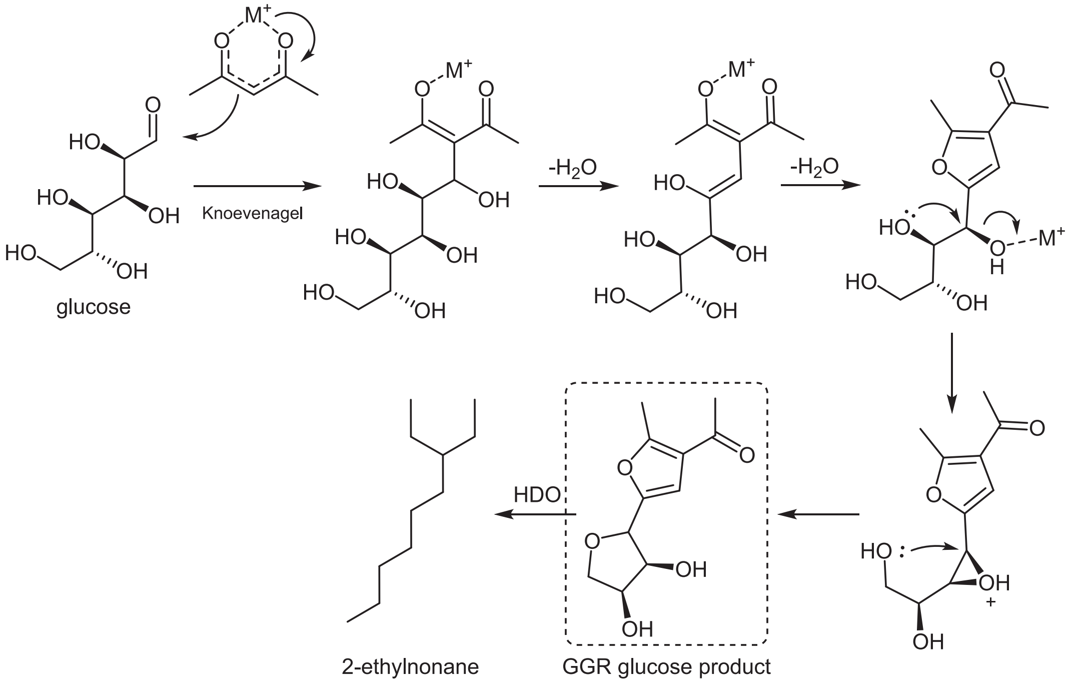

Fig. 7. García-González Reaction (GGR) ad follow-up upgrading.

pyrolysis, gasification, and liquefaction are widely utilized for their operational simplicity and ability to process materials such as agricultural residues, forestry waste, municipal solid waste, and algae [251]. These methods are particularly effective for converting low-value biomass into intermediate products like pyrolytic liquids with enhanced fuel properties. However, challenges such as high water content in feedstocks and the need for further upgrading of pyrolytic liquids highlight areas for improvement. Recent innovations, such as hydrothermal methods — including Aqueous Phase Reforming (APR), hydrothermal liquefaction (HTL), catalytic hydrolysis (CH, described earlier), and pyrolysis [252] — have addressed these limitations. These processes operate under water-compatible conditions, reducing dehydration energy costs and making them well-suited for hydrophilic substrates like mono- and polysaccharides.

Reforming. Biomass reforming processes involve the complete gasification of substrates into synthesis gas (syngas), an industrially versatile mixture of carbon monoxide (CO) and hydrogen (H_2). Syngas, commonly obtained by reforming of hydrocarbons (Eq. (1)), is a pivotal intermediate in the production of a wide range of fuels, oxygenates, and high-volume chemicals such as formaldehyde and acetic acid. Reforming followed by the water–gas shift (WGS) reaction (Eq. (2)), a process collectively known as steam reforming, is a well-established method for hydrogen production.

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2 \tag{1}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{2}$$

Syngas can also be transformed into a wide range of valuable products, including methane, methanol, ethanol, *iso*-butanol, dimethyl ether, and methyl-*tert*-butyl ether [253]. Today, methanol is produced exclusively on an industrial scale through the catalytic conversion of syngas (Eq. (3), at relatively mild conditions (50–100 bar, 200–300 °C) [254].

$$CO + 2H_2 \rightleftarrows CH_3OH \tag{3}$$

Methanol is indeed a highly promising fuel for certain applications, such as direct methanol fuel cells (DMFC) [255]. However, its direct use in ICEs is limited by several unfavorable properties, including low energy density and incomplete miscibility with hydrocarbons (as discussed later). A viable alternative for use of methanol in ICEs is to use its dehydration product dimethyl ether (DME) (Eq. S1), featuring enhanced, LPG-like combustion characteristics [256] (see later). The synthesis of higher alcohols from syngas has been practiced for over a century, utilizing modified methanol catalysts. Depending on the catalytic system employed, mixed alcohols (from C1 to C8) can be produced either directly from syngas or via methanol intermediacy [257]. Another prominent and well-established syngas conversion technology is the Fischer-Tropsch (FT) process (Eq. (4)).

$$nCO + 2nH_2 \rightleftarrows C_nH_{2n+1} + (n-1)H_2O \tag{4}$$

High-purity hydrocarbons, including LPG (C3–C5), gasoline (C5–C12), diesel (C13–C22), and waxes (C23–C33) can be obtained through this process. The products distribution is highly dependent on the employed catalyst, operating temperature, pressure, and the H_2/CO feed ratio [258].

The complete bond breaking of carbohydrates during reforming (Eq. (5)) is associated with a significant enthalpic increase, requiring substantial energy input (e.g., ~150 kcal mol^{-1} for glucose steam reforming).

$$C_nH_{2y}O_n \rightleftarrows nCO + yH_2 \tag{5}$$

Nevertheless, carbohydrate reforming exhibits a greater thermodynamic gain at low temperatures, compared to the reforming of methane or other alkanes (Eq. (1)). In other words, while steam reforming of alkanes is only thermodynamically feasible ($\Delta G°/RT < 0$) at temperatures above 675 K (above 900 K for CH_4), the reforming of oxygenated hydrocarbons like carbohydrates provides a viable low-temperature pathway for generating CO and H_2 (Fig. 8) [259].

Moreover, the liquid-phase WGS reaction is more favorable than its gas-phase counterpart at low temperatures (> ~400 K). Building on these insights, the APR process was developed, a catalytic reforming-WGS process devoted to H_2 production under mild conditions, typically at temperatures of 150–250 °C and pressures of 10–50 bar [260]. This method is particularly appealing for its ability to directly process carbohydrate-rich solutions, reducing the need for extensive dehydration steps. Typical feedstocks for APR are oxygenated compounds with a carbon-to-oxygen ratio of 1:1, such as polymeric or oligomeric sugars, and poly- or oligo-alcohols (e.g. those derived from carbohydrates through HDO). Various metal catalysts have been studied to tailor the process towards H_2 and/or alkanes. A key feature of APR is its ability to generate CO-free H_2, which is directly suitable for use in polymer electrolyte membrane fuel cells.

Selective **hydrogenation** and **HDO**, akin to the hydro-treating processes used in petroleum refineries, encompasses a suite of methods designed to remove oxygen from carbohydrates or from polyols. Extensive application of catalysis enable these processes to operate at relatively low temperatures (100–250 °C) [238]. The sustainability of the process can be enhanced by sourcing the hydrogen required for HDO from the APR of carbohydrates. Mild HDO of carbohydrates yield polyols, which are highly valuable in the polymer industry. In contrast, more intensive HDO processes, produce hydrocarbons that can be seamlessly blended with existing fuel infrastructures. Diverse applications of HDO processes are discussed in Section 3.1.

Guerbet-like processes, encompassing the alkaline oxidative coupling of alcohols followed by reduction, represent a class of mild thermochemical methods operating within a temperature range of 180–360 °C. These processes aim to produce elongated carbon-chain products such as fatty alcohols, ethers, or alkanes from smaller alcohols or polyols. The reaction involves the initial oxidation of a starting alcohol to the corresponding aldehyde, which subsequently undergoes aldol condensation. The intermediate enone is then reduced to yield branched, longer-chain alcohols (Fig. 9) [261]. For instance, starting with ethanol, medium-chain alcohols such as *n*-butanol, *n*-hexanol, 2-ethylbutanol, and 2-ethylhexanol can be synthesized [262].

By implementing a more rigorous reductive step, a broader spectrum

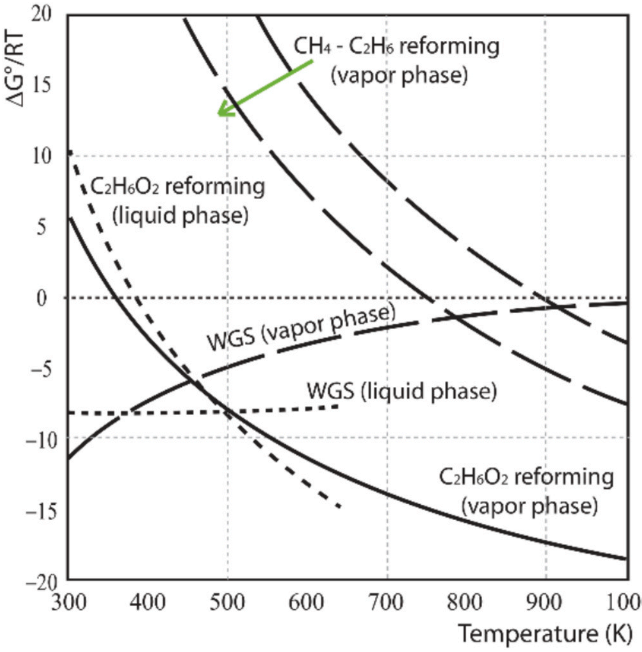

Fig. 8. Standard Gibbs energy for reforming and WGS processes. Adapted from Ref. [259].

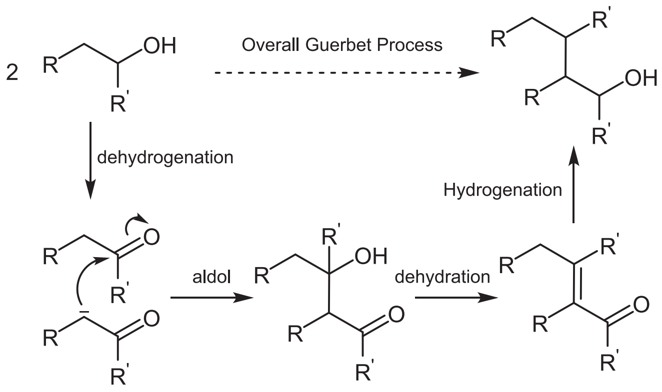

Fig. 9. Simplified scheme of the Guerbet process.

of low-oxygen-containing compounds can be accessed, including alkanes [263]. Recent advancements have highlighted the synergistic role of catalysts featuring both acidic and basic sites on their surfaces, which enable the process to operate under milder conditions [264,265].

Hydrothermal Liquefaction (HTL) directly converts wet biomass into bio-oil under near- or super-critical water conditions (200–400 °C, 100–300 atm), without the need for prior drying. HTL thus offers a distinct advantage compared to pyrolysis, which typically works on dry biomass. Compared to pyrolysis-derived bio-oils, HTL stands out for its high yield (up to 80%) and high energy density of the produced bio-oil [266,267], which benefits of simpler follow-up processing towards biofuels [268]. HTL involves several simultaneous water-mediated processes, including depolymerization, hydrolysis, dehydration, thermal deamination, and decarboxylation. These processes contribute to the rearrangement of newly formed hydrophilic monomers into water-insoluble bio-oil. Additionally, at extended times and temperatures, there is a tendency for repolymerization into char [269]. Therefore, the selectivity and yields towards definite HTL products rely on the specific process conditions [270], catalysts, and pH of the mixture [271]. Operating at 400 °C, HTL of cellulose mostly produce glucose at short reaction times, while glycolaldehyde, pyruvaldehyde, and glyceraldehyde dominate, at longer reaction times [272]. In other conditions and working at 200 °C, glucose and LGA (Fig. 4) are main cellulose HTL products [271].

Low-Temperature Carbonization (LTC) and **Catalytic Hydrothermal Carbonization** (CHTC) are innovative techniques, operating at moderate temperatures (180–250 °C) and under mild pressures on wet biomass, and able to produce solid biochar. Biochar produced through LTC and CHTC is a versatile material with applications spanning energy, agriculture, and industry. Biochar represents a renewable solid fuel [273], offering higher energy density and improved stability compared to raw biomass, resulting in a more efficient combustion, reduced emissions, and easier transportation. Biochar's compatibility with existing solid fuel infrastructure, such as boilers and stoves, enables its adoption without significant technological modifications. Biochar is also widely recognized as an effective soil amendment, enhancing soil structure, nutrient retention, and microbial activity, thereby improving crop yields [274]. In industrial settings, biochar has been explored for co-firing in power plants, syngas production [275], and metallurgical processes [276,277]. The high intrinsic porosity of biochar, which can be tailored by optimizing process parameters, makes it an ideal precursor for activated carbon production, which is extensively used in water purification, gas adsorption, and industrial catalysis [278].

3.3. *Bioconversion of carbohydrates*

The bioconversion of carbohydrates is based on the metabolic capabilities of microorganisms and fungi to transform carbohydrate-rich feedstocks into biofuels and other valuable products [279]. These transformations exhibit remarkable versatility, depending on the substrate type, the microorganism or enzymatic system utilized, and the specific biochemical pathways driving the conversion. Biological processes are particularly valued for their high selectivity and ability to operate under mild conditions, significantly reducing energy requirements and operational costs compared to thermochemical (Section 3.2) or chemical (Section 3.1) methods. In addition, the conversion of carbohydrates into other fermentable substrates can extend the application of bioconversion technologies. A notable example is the hybrid thermo-biochemical process involving the carbohydrate reforming (Eq. (5)), followed by bioconversion of syngas, which is based on the availability of microorganism capable to metabolize syngas. For instance, ethanol, 1-propanol, and 1-butanol have been successfully produced via syngas fermentation using a mixed culture of *Alkalibaculum bacchi* and *C. propionicum* [280].

The conversion of biomass-derived carbohydrates into C1–C4 alcohols is regarded as one of the most advanced and promising short-term strategies for producing biofuels, contributing significantly to the renewable energy transition in the transportation sector. While methanol can be efficiently produced via the thermochemical conversion of syngas (Eq. (3)), several established bioconversion processes involves the microbial fermentation of monomeric or oligomeric carbohydrate feedstocks to produce C2–C4 alcohols [281]. First-generation bioethanol (Section 2.1) is the most established and widely used alcoholic biofuel [282]. Its production relies on the fermentation of sugars, a process extensively employed in the beverage industry for over a century [283]. Yeasts, particularly strains of *Saccharomyces cerevisiae*, *S. uvarum*, and *Candida utilis*, serve as the primary microorganisms for the biocatalytic conversion of sugars into ethanol. These yeasts efficiently metabolize hexoses under anaerobic conditions, following the Gay-Lussac equation (Eq. S2), achieving a theoretical maximum yield of 0.51 g of ethanol per gram of glucose [284]. However, pentose fermentation is limited to specific yeast strains and is characterized by lower productivity, posing challenges for the efficient utilization of LC feedstocks in advanced bioethanol production.

During glycolysis, glucose is broken down into pyruvate, generating ATP and NADH. In the absence of oxygen, pyruvate undergoes decarboxylation to form acetaldehyde and CO_2 [285]. Acetaldehyde is subsequently reduced to ethanol by alcohol dehydrogenase, regenerating NAD^+ to sustain glycolysis [286].

Despite its potential, several factors limit the efficiency of carbohydrate fermentation. These include the sensitivity of microorganisms to various inhibitors, such as ethanol itself [287], byproducts from biomass hydrolysis (e.g., FA, 5-HMF, phenolics) [288], high sugar concentrations and associated osmotic stress [289].

Second-generation bioethanol is gaining traction, while third-generation bioethanol production remains limited to laboratory and pilot-scale stages [290].

To evaluate the suitability of C1–C4 alcohols as fuels, it is essential to compare their key physical and chemical properties with those of conventional fossil fuels (Table 1).

Lighter alcohols generally have low energy densities (lower heating value) and limited miscibility with hydrocarbons (lower log P) [186], which makes their direct use as fuels challenging. Methanol, in particular, is rarely blended with conventional fuels or used directly in ICEs. Instead, it is typically converted into DME (Eq. S1), a more practical alternative that serves as an ideal fuel for heavy-duty compression ignition engines [256]. Despite its limitations, ethanol is widely used as a gasoline additive, particularly in the U.S. and Brazil. In the Netherlands, E15 blends (15% ethanol) are available, while E20–E25 blends are primarily distributed in Brazil [291]. Lighter alcohols are better suited for direct use in DMFCs [255] or molten carbonate fuel cells [292], expanding their applicability to stationary energy systems.

Among C1–C4 alcohols, propanols and butanols exhibit superior fuel properties (see Table 1), including better miscibility with hydrocarbons, higher energy density, and lower hygroscopicity compared to methanol

Table 1
Physicochemical properties of alcohols, compared to ordinary fuels. Adapted from Ref. [281].

	Methanol	Ethanol	Propanols	Butanols	DME	Gasoline	No.2 Diesel Fuel
Formula	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH	CH_3OCH_3	C_5-C_{12}	$C_8 - C_{25}$
Molar Mass (g/mol)	32.04	46.07	60.10	74.12	46.07	100–105	~200
Octanol/water partition (log *P*)	− 0.77	− 0.31	0.15	0.65	0.10	3.5	~6.0
d at 20 °C (g/cm^3)	0.79	0.79	0.785–0.803	0.787–0.81	0.67*	0.72–0.77	0.82–0.84
bp at 1 atm (°C)	64.6	78.4	82 – 97	83 – 118	−25	27 – 225	188 – 343
Flash Point (°C)	14	13	12–15	11–35	−41	~45	> 55
Autoignition Temp (°C)	470	425	371–339	343 – 470	235	257	316
Air-Fuel Ratio	6.5	9	10.2	11.2	9	14.6	14.5
Heat of vaporization (MJ/kg)	1.2	0.92	0.75	0.61	0.47	~0.36	~0.26
Lower heating value (MJ/kg)	19.7	26.7	30.6	34.4	28.4	43.4	43

* Compressed at 5 bar.

and ethanol. These characteristics make them highly promising biofuels that can be directly used in existing ICEs without significant modifications. Additionally, blending propanols with gasoline has been shown to reduce pollutant emissions [293] while improving engine performance parameters such as power output and fuel efficiency [294]. Similarly, butanol has been successfully blended with diesel in substantial proportions, leading to significant reductions in smoke density, NO_x, and CO emissions [295] while maintaining comparable engine performance. Butanol offers additional advantages: it enhances fuel resistance to water contamination, allows for higher blending concentrations without requiring vehicle modifications, and readily dissolves in vegetable oil-derived fuels (e.g., biodiesel) at any ratio, thereby reducing viscosity [296].

Unfortunately, compared to ethanol and butanols, the pathways for producing 1-propanol and 2-propanol are significantly less developed [297]. Although fermentation processes capable of generating 1-propanol and/or 2-propanol have been reported [298], their yields remain limited. Certain bacteria, such as various *Clostridium* strains, can metabolize oligosaccharides directly into 2-propanol through isopropanol-butanol-ethanol (IBE) fermentation, which follows a metabolic pathway similar to that of acetone-butanol-ethanol (ABE) fermentation [299]. However, in both processes, butanol is the predominant product. An innovative, nature-inspired strategy to address the limitations of monoculture involves the use of artificial co-cultures. These systems synergistically combine metabolic pathways from different microorganisms to enhance propanol production efficiency [300]. Additionally, genetic and metabolic engineering offer promising approaches to improve the propanol-producing capabilities of microorganisms [301–305]. For instance, an engineered strain of *Thermobifida fusca* has demonstrated the ability to directly convert lignocellulosic material into 1-propanol [306].

The microbial ABE process was among the first large-scale industrial fermentation methods with global significance for 1-butanol production [282]. Initially commercialized over a century ago, it expanded significantly during World War I due to the demand for acetone [307], a key ingredient in the production of Cordite, a smokeless firearm propellant. By the early 20th Century, the ABE process was the second-largest fermentation process worldwide, surpassed only by ethanol fermentation. However, the emergence of efficient chemical synthesis methods, such as the oxo, Reppe, and Guerbet processes (Fig. 9), made butanol production from fossil resources or bioethanol more economically viable [308]. Although its popularity declined after the 1950s, the ABE process has regained interest for biofuel and biochemical production [309], driven by EU REDII directives promoting sustainable energy. The saccharolytic and amylolytic bacterium *Clostridium acetobutylicum* metabolize starch, monosaccharides, and disaccharides (both hexoses and pentoses) in a two-phase process. During the initial acidogenic phase, monosaccharides are converted into hydrogen, CO_2, acetate, and butyrate during biomass growth. A drop in pH triggers the stationary (solvogenic) phase, during which fermentation products are formed using intermediates from the first phase, up to inhibitory concentrations [310]. Butanol, being hydrophobic nature and membrane-disruptive, is the most toxic product, limiting microbial growth and production efficiency. ABE-producing microorganisms are more sensitive to inhibitors generated during LC biomass pretreatment, such as FA, 5-HMF, and phenolics, compared to yeast strains used for ethanol production [311]. A typical ABE fermentation yields acetone, butanol, and ethanol in a 3:6:1 mass ratio [312], along with byproducts such as CO_2, H_2, and organic acids (e.g., lactic acid, acetic acid, and butyric acid) [313]. From 100 kg of starch, the ABE process typically produces 11 kg of acetone, 22.5 kg of butanol, 2.7 kg of ethanol, 60 kg of CO_2, and 2 kg of H_2. Despite its potential, industrial-scale biobutanol production faces economic challenges similar to those in advanced bioethanol production, including biomass pretreatment, inhibitors removal, saccharification, fermentation, and product recovery. Promising results have been achieved in ABE fermentation of wheat straw acid hydrolysates using *Clostridium beijerinckii* [314], though alkaline pretreatment can generate inhibitory salts requiring removal [315]. Additionally, municipal waste streams [296,316] and carbohydrate-rich algae have been explored as alternative feedstocks for biobutanol production [317]. Enhanced butanol yields can be achieved through continuous solvent stripping during fermentation to reduce product inhibition [318]. Advances in microbial strain development, particularly through metabolic and genetic engineering, aim to improve butanol tolerance and production efficiency [319,320]. Syngas fermentation offers an alternative pathway for butanol production, utilizing microorganisms capable of metabolizing CO as a carbon source [321].

Carbohydrate-rich biomass can also be converted into biofuels and biochemicals through other processes. Anaerobic digestion, or methane fermentation, breaks down organic matter in the absence of oxygen, producing biogas — a mixture primarily composed of CH_4 and CO_2 [322]. This process involves four stages: (i) Hydrolysis, where complex organic materials are broken down into simpler molecules such as sugars, amino acids, and fatty acids; (ii) Acidogenesis, where these molecules are converted into volatile fatty acids (VFAs), alcohols, and gases (e.g. H_2 and CO_2) (iii) Acetogenesis, where VFAs and alcohols are transformed into acetic acid, H_2, and CO_2; and (iv) Methanogenesis, where methanogenic archaea convert acetic acid and H_2 into methane and CO_2 [323].

Anaerobic digestion can be operated under varying conditions, with mesophilic digestion (moderate temperatures) being the most energy-efficient option [324]. This versatile process can tolerate both high-moisture feedstocks [325], such as food waste and sewage sludge [326,327], and dry feedstocks [328], such as animal manure [329]. Two-stage anaerobic digesters, which optimize conditions for both acidogenic and methanogenic bacteria, are increasingly used to enhance performance [330]. Adding biochar as a biomass additive has shown potential for absorbing inhibitory compounds and improving buffering capacity [331].

Dark fermentation is a related process focused on biohydrogen production [332]. Unlike anaerobic digestion, dark fermentation suppresses methanogenesis to prevent methane formation, facilitating hydrogen accumulation. Strategies to inhibit methanogens include acid or heat treatments of microbial inoculum [333], reducing hydraulic retention time [334], and modifying reactor configurations [335]. Central to dark fermentation are anaerobic bacteria, particularly *Clostridium* species [336]. However, challenges such as VFA accumulation, hydrogen-consuming microorganisms, and the need for efficient downstream gas purification complicate the process [337].

In addition to biofuels, carbohydrate bioconversion is essential for producing PCs used in various industries, such as acetic acid [338], citric acid [339], and lactic acid [340].

3.4. Other methods of carbohydrate conversion

In addition to bioconversion, thermochemical, and chemical conversion, other emerging methods are being explored for the transformation of carbohydrates into biofuels.

The electrochemical conversion of carbohydrates into upgraded chemicals is not a new concept [341]. However, recent research has predominantly focused on the electro-generation of glycosyl radicals and subsequent coupling processes [342], as well as the selective anodic oxidation of primary [343] or secondary [344] hydroxyl groups. A primary appeal of oxidative processes lies in their ability to couple these reactions with hydrogen generation at the cathode [345]. Prolonged electrolysis of glucose, for instance, can yield formic acid [346], which may also be further upgraded through bioconversion [181].

Shifting to the more intriguing topic of carbohydrate reduction for biofuel production, electroreduction of carbohydrates is a long-known but largely overlooked method [347]. Nevertheless, its potential for industrial application remains significant. A notable example is the production of alditols, currently obtained exclusively through high-pressure hydrogenation of carbohydrates. Sorbitol (Fig. 5), the hydrogenation product of glucose, exemplifies this potential. Although the electroreductive approach was once successfully scaled up for industrial use [348], it gradually lost attention until its recent resurgence [349,350]. Renewed interest in this method should now focus on achieving new levels of efficiency, potentially integrating both reductive and oxidative upgrading processes to maximize output and utility.

Photoelectrochemical systems, which utilize both light and electricity to drive carbohydrate conversion, are also being actively developed [351]. Additionally, hybrid systems that combine biological and chemical processes, such as bio-electrochemical reactors [352], are emerging as promising approaches. These systems aim to leverage the strengths of both methodologies to enhance the efficiency and sustainability of biofuel production.

4. Conclusions

Humanity is increasingly recognizing the need to align its development with the carbon cycle. Embracing CO_2 as a fundamental, renewable carbon resource presents a transformative opportunity to drive sustainable development through the CE. This approach enables a progressive and sustainable transition within our carbon-based economy while supporting the broader energy shift. Exploiting nature-based processes to convert CO_2 into carbohydrates not only contributes to atmospheric CO_2 reduction but also represents one of the most reliable and integrable solutions for harmonizing agricultural and industrial activities with sustainability goals.

The development of diverse carbohydrate-producing factories offers significant opportunities to establish value chains that support local economies while avoiding the food-versus-fuel dilemma. Advances in low-energy-input carbohydrate processing technologies will enable the integrated production of affordable biofuels and carbon-based materials, benefiting from economies of scale. Carbohydrate-derived biofuels are highly compatible with existing liquid fuel infrastructures and industrial energy systems, including ICEs, ensuring a smooth transition without costly infrastructure overhauls.

The CE also fosters synergies with emerging low-carbon energy technologies. For example, the availability of green hydrogen will enable cost-effective hydrogenation and HDO processes, producing energy-dense, deoxygenated biofuels. Conversely, APR of carbohydrates could supply biohydrogen, supporting the development of the hydrogen economy. A related opportunity lies in the use of carbohydrate-derived bioalcohols in DMFCs and molten carbonate fuel cells, effectively serving as carbon-based hydrogen carriers. Additionally, valuable interactions exist between the CE and CO_2ER. For instance, syngas derived from carbohydrate reforming offers a transitional solution for sourcing reduced C1 carbon compounds while industrial-scale CO_2ER technologies are still under development. Conversely, directing CO_2 streams produced from anaerobic carbohydrate bioconversion processes into electroreduction pathways could enable the co-production of valuable C1 compounds — such as carbon monoxide, formic acid, methanol, and methane — which serve as key feedstocks for various thermochemical and biochemical biofuel conversion pathways. This integrated approach promises to enhance overall efficiency and overcome the carbon conversion limitations inherent in purely bioconversion processes.

Such innovations, grounded in the CE, are paving the way for next-generation renewable biofuels, biochemicals, and biomaterials, advancing the broader goal of sustainable carbon utilization and a circular bioeconomy. Advancements in the CE have the potential to significantly reduce dependence on fossil carbon resources and promote more equitable energy and income distribution, fostering a society better equipped to address the interconnected challenges of climate change, resource depletion, and growing energy demands.

CRediT authorship contribution statement

Fabrizio Roncaglia: Writing – review & editing, Supervision, Project administration, Conceptualization. **Alberto Ughetti:** Writing – original draft. **Andrea Severini:** Writing – original draft, Visualization. **Nicola Porcelli:** Writing – original draft. **Marco Mazzali:** Writing – original draft. **Veronica D'Eusanio:** Writing – review & editing, Supervision. **Luca Rigamonti:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seta.2026.104880.

Data availability

No data was used for the research described in the article.

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