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Review

Carbon emissions and decarbonisation: The role and relevance of fermentation industry in chemical sector

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ABSTRACT

Fermentation industry is emerging as sustainable technological alternative to cater the production of various chemical building blocks which are commercially manufactured by petrochemical route. The primary reason for this major transition is global commitment towards decarbonisation of chemical sector, as their conventional fossil-based routes pose serious environmental threat. For instance, in 2022, the direct carbon dioxide (CO_2) emission during synthesis of primary chemicals accounted for ~ 920 Mt. CO_2 is one of the prominent greenhouse gases (GHG's), contributing majorly towards global warming effect and drastic climate change. Fermentation industry largely thrives on exploiting fermentable and organic carbon derived from edible and/or non-edible biomass and transforming them to valorised products using microbial cell factories. Therefore, the production of bio-based chemicals via this route is often associated with low or zero-carbon footprint, resulting in either carbon neutral or carbon negative products. This review focuses on different types of fermentative processes and their impact on carbon release and decarbonisation. It further discusses the relevance and contribution of fermentation industry as well as biological processes to provide a sustainable solution towards decarbonisation of chemical sector. Further, it showcases the advantages of some commercial proven and/or pipeline bio-based products over their conventional competitor fossil-based products, especially from an environmental viewpoint. Finally, advantages of biogenic CO_2 from fermentation industry over other sources and CO_2 removal from fermentation as a platform for carbon offsetting are covered.

1. Introduction

Carbon dioxide (CO_2) has been the most rampant greenhouse gas (GHG)and its level in atmosphere has increased by ~ 50 % since the start of industrial evolution [1]. The total energy GHG emissions in 2022 were 41.3 gigatonnes CO_2 equivalents (Gt-CO_2e), in which CO_2 was the single largest and most significant contributors (89.1 %) [2]. Its global radiative forcing in 2022 was 2.17 W/m^2 compared to 0.65, 0.274 and 0.193 W/m^2 exerted by methane, chlorofluorocarbons and nitrous oxide, respectively, a major cause of disturbing climate equilibrium [3].

Abbreviations: AD, Anaerobic digestion; 2,3-BDO, 2,3-Butanediol; 1,4-BDO, 1,4-Butanediol; 1,3-BG, 1,3-Butylene glycol; 1,3-PDO, 1,3-Propanediol; CAGR, Compound annual growth rate; CCS, Carbon capture and storage; CDR, Carbon dioxide removal; CRI, Carbon recycling international; DAC, Direct air capture; EOR, Enhanced oil recovery; GHG, Greenhouse gases; GTL, Gas-to-liquids; 3-HP, 3-Hydroxypropanoic acid; LA, Lactic acid; LCA, Life cycle assessment; MES, Microbial electrosynthesis; NET, Net emissions technology; PHA, Polyhydroxyalkanoic acid; PHB, Polyhydroxybutyrate; PE, Polyethylene; SA, Succinic acid; SDG, Sustainable development goals; TCA, Tricarboxylic acid; USD, US dollars.

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The CO_2 levels in atmosphere never exceeded beyond 300 ppm in pre-industrial revolution era, was 315 ppm in 1958 but unprecedentedly reached 419 ppm in 2022. In May 2023, CO_2 levels hit 424 ppm which is a new record, an alarming situation. If the continuously increasing energy demand is met largely by fossil fuels, the atmospheric CO_2 levels could be 800 ppm or higher by the end of this century, an unseen condition in last 50 million years [4,5]. Thus, impact of CO_2 on climate change can be more deleterious, and therefore, decarbonisation is the need of the hour [6,7]. During the Paris agreement in 2015, many nations across the world have signed the pact to decarbonise and reduce GHG emissions. In fact, legislative pressure in many countries across the world is pushing energy and chemicals industries away from fossil-based routes [8,9].

Until the last two decades, petrochemical route was the primary market driver for manufacturing of transportation, domestic fuels, and numerous commercially important bulk, platform and speciality chemicals [10,11]. The main reasons for heavy reliance on oil-sector included low manufacturing cost, high profit margins, availability of technical knowledge on how to maximally exploit each and every stream of crude/refined oil and their transformation into variegated products via chemo-catalytic route. At the cost of rapid industrial development, issues such as high energy usage, generation of non-degradable wastes and burden imposed on environment during the production of these chemicals were neglected or ignored. However, gradually it was realised that this conventional industry that mainly thrived on fossil resources is unsustainable, as the feedstock used is non-renewable in nature. Further, the prices of crude oil are dynamic and volatile in nature, and the processing associated with it deleteriously impacted the environment. One of the hazards posed by the petrochemical industry is its contribution to GHG emissions, one of the main contributors to global warming and visible output as climate change [12–14]. For instance, in 2022, during the primary chemical production, ~920 Mt of direct CO_2 was released [15]. The adverse impact on the environment can easily be adjudged by the forecast made by the Statistical Research Department, which anticipates that the GHG emissions from petrochemical industry will reach 2.8 billion metric tons of CO_2 equivalents ($MtCO_2e$) by 2030 [16]. If this scenario is left unattended, it will deter the unified goal of nations to restrict the rising global temperatures to 1.5 °C, under the Paris agreement [8,13]. The high environmental cost of petrochemical routes motivates the development of cleaner and economical biological routes for manufacturing chemical building blocks. One of the sustainable technology options to immediately enforce decarbonisation is switching from fossil-based route to cleaner and commercially viable biotechnological processes using renewable feedstocks for manufacturing chemical building blocks, including fuels and chemicals [17]. In this regard, last decade has witnessed unwavering efforts to drive technical innovations using sustainable approaches, choosing and leveraging upon affordable technologies, nurturing right partnerships and conscious government initiatives across the globe. As a result, there has been continuous rise in bio-based products market demand. According to a recent report, market of bio-based chemicals was 128.5 billion USD in 2022, which is predicted to reach 271.7 billion USD by 2031 with a compound annual growth rate (CAGR) of 9.2 % [18].

The use of renewable biomass is the key to achieve low carbon economy and represents one of the most viable and sustainable option to align with the UN Sustainable Development Goals (SDG). In industrial biotechnology, we directly or indirectly make use of carbon dioxide because the feedstocks originate either from the plant biomass or are synthesized by CO_2 fixing autotrophic organisms [19]. Theoretically speaking, CO_2 is ubiquitous in nature, which if fixed into stable organic compounds is carbon neutral, but if exists in free form contributes to global warming. For instance, biomass is renewable and infinite resource of organic carbon that comprises principally of plants and large group of autotrophic microbes which can fix CO_2 from different sources such as flue gas as well as eliminate CO_2 from the atmosphere, owing to the presence of photosynthetic machinery, and store it primarily in the form of polysaccharides. Therefore, unlike the fossil energy sources, when biomass is used as an energy source using chemical, thermo-chemical or biological platforms, the carbon lost in the form of CO_2 is re-sequestrated back biologically by the plants or micro/macro algae making it carbon neutral. Thus, decarbonisation is anticipated to occur by adopting sustainable approaches such as shifting from fossil-based resources to renewable biomass and choosing microbial fermentation for biomass valorisation, a promising way for cleaner production of bio-based chemicals.

Fermentations are biological processes where metabolic pathway of any microbe is tweaked in such a way that it results in efficient over-production of industrially important metabolites, using biomass-derived renewable and fermentable carbon as their primary energy source. In fact, there is a long history of microbial cell factories using renewable feedstocks (especially rich in fermentable sugars) and bio-transforming them into metabolites with commercial potential and multitude of applications. For example, the potable ethanol manufacturing is an age-old established process which is marketed under different trade names such as wine, whisky, beer etc. Besides ethanol, currently, there are a good number of marketable products (platform chemicals, biofuels, polymers etc,) that are coming from biological or bio-based routes with biomass as a starting material, such as 1, 3 – propanediol (1,3-PDO), polyhydroxyalkanoates, lactic, succinic, citric and itaconic acid, etc. Since the raw material for cell factories such as bacteria, yeast, algae or fungi is biogenic in nature, degradation/oxidation of these products recycle CO_2 back into the environment. Therefore, these products are considered as net-zero and contribute to a carbon–neutral society. But it is equally necessary to closely watch that how rapidly the carbon is recycled back into the biosphere. The best scenario is if we could retain the CO_2 in captured form as long as possible which will be considered as greenhouse gas removal. This review focuses on the role and relevance of fermentation industry towards carbon emission and in decarbonizing chemical sector, showcasing the advantages of some of the commercially proven and/or important pipeline bio-based products over their conventional competitor fossil-based products, especially from the environmental viewpoint.

2. Types of fermentation processes

Keeping CO_2 as a centre-stage molecule, fermentation products can be divided into three categories: those where CO_2 is released concomitantly as a byproduct; those where main product is formed without any carbon loss in the form of CO_2, and lastly, which include CO_2 sequestration as a substrate or co-substrate using distinct and unique biochemical pathways. This is also reflected in yields of their products as shown in Table 1, which demonstrates the product yields from glucose as representative feedstock via microbial fermentation. The succeeding section gives a brief overview of these commercially scalable fermentation products.

2.1. Fermentation products with loss of CO_2

The metabolic routes for many products involve decarboxylation steps, which not only reduce the product yield, but also let the CO_2 to go back to the atmosphere rapidly and easily (Fig. 1). The two best examples in this category are ethanol and 2,3-butanediol (2,3-BDO). In the commercial-scale, ethanol and 2,3-BDO are produced through both petrochemical and fermentative routes. In the latter approach, ethanol production is accompanied with substantial carbon loss in the form of CO_2. The stoichiometric equation for ethanol production from glucose is $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ [20,21]. During the manufacturing of one liter of beer and wine, 35 and 87 g of CO_2 is released, respectively [22,23]. Europe, despite being not a big player in ethanol production, releases 5.71 and 1.44 Mt CO_2/year during bioethanol fermentation and beer production, respectively [23]. The annual global ethanol production is > 100 billion liters, indicating release of ~ 70–80 Mt CO_2 only

Table 1
Comparison of bio-products yields and loss/assimilation of CO_2on glucose as substrate.

Product	Theoretical yield (g/g)	CO_2 loss/assimilation (mole/ mole glucose)
Ethanol	0.51	−2
2,3-Butanediol	0.50	−2
1,3-Butanediol	0.50	−2
1,4-Butanediol	0.50	−2
Succinic acid (oxidative TCA cycle)	0.66	−2
Itaconic acid	0.72	−1
Lactic acid	1.00	0
1,3-Propanediol	0.84	0
3-Hydroxypropionic acid	1.00	0
Citric acid	1.07	0
Succinic acid (reductive TCA cycle)*	1.31	+2
Fumaric acid (reductive TCA cycle)*	1.29	+2
Malic acid (reductive TCA cycle)*	1.49	+2

Note: *Yield is based on assumption that CO_2 for carboxylation is provided from external source. + Represents CO_2 fixation/capture; - represents CO_2 released/lost.

from ethanol industry. This number will increase much more as ethanol production is projected to 164 billion liters by 2030 [20,21]. The carbon loss during ethanol production in the form of CO_2 is unavoidable. But at the same time it is of high purity (99 %) and the gaseous stream mostly contains moisture and traces of organic and sulphur compounds [24]. Therefore, in many wineries, breweries, sugarcane, and corn ethanol industries simple technologies like CO_2 capture technology is adopted, where biogenic CO_2 is captured by trapping the outlet gaseous stream of fermentation through foam traps and dehydrated to remove water. Volatile and other impurities are removed through scrubber followed by compressing CO_2 for storage [25].

Similarly, in case of 2,3-BDO, one third carbon is lost as CO_2: $C_6H_{12}O_6 \rightarrow C_4H_{10}O + 2CO_2$ [26]. This loss of CO_2 not only restrict product yield close to ~ 0.50 g/g but quickly release the captured CO_2 into the environment. In present time, a number of companies such as Global Bio-Chem Technology Group, Biosyncaucho S.L., GS Caltex Corporation, etc are producing 2, 3-BDO, commercially via fermentative route [27]. Though the details of CO_2 emissions from the bio-based 2, 3-BDO plants is unavailable in public domain, but bio-based companies have shown superiority over fossil-based route, in terms of environmental sustainability. For instance, GS Caltex, a Korean based company is producing 2, 3-BDO since 2019 at its demonstration facility and selling its product under the trade name GreenDiol^{TM} [28]. The company claims that their bio-based 2,3-BDO has competitive edge over oil-based route, as it can contribute to 40 % lower GHG emissions and energy usage [29]. Like ethanol and 2,3-BDO, there are a number of products with similar fate. For example, n-butanol & poly-hydroxyalkanoates (PHA) generated via acetyl-CoA and the products obtained from oxidative TCA cycle such as α-keto glutaric, succinic, fumaric and malic acid are accompanied with CO_2 loss. Similarly, 40 % carbon is lost as CO_2 during biomethane production via anaerobic digestion (AD): $CH_3COOH \rightarrow CH_4 + CO_2$ [23,30].

2.2. Fermentation products with no loss of CO_2

Here, we discuss about the metabolic products without any loss of carbon i.e., all the available carbon present in the substrate is conserved in the product. One of the best examples is lactic acid (LA) and two moles of LA are produced from one mole of glucose during homo lactic acid fermentation [31,32]. Since there is no loss of carbon during synthesis of LA, all the carbon from substrate is conserved in product leading to a conversion yield of 1.0 g/g which is almost double than ethanol with ~ 33 % carbon loss as CO_2. In the current time, about 70 % of LA is manufactured via microbial route [33]. LA is not a biofuel but a platform chemical with enormous applications where renewable carbon is trapped in product form for a long time. Similarly, 1,3-PDO and 3-hydroxypropionic acid (3-HP) are formed from glycerol as well as glucose without any loss of CO_2. Like LA, 1,3-PDO is also manufactured commercially via biological route from glucose or glycerol [34,35]. In 2015, Argonne Laboratories conducted the cradle to grave analysis of ten different bio-products against their fossil-based counterparts, using their GREET module. They found that glycerol-derived 1,3-PDO and corn-derived L(+) LA led to 64 and 49 % lesser GHG emissions compared to their fossil-based route. Furthermore, the fossil fuel consumption during fermentation for the glycerol derived 1,3-PDO and corn-derived LA was 61 and 46 % lesser than conventional oil-based route, respectively [36].

2.3. Fermentation products with capture of CO_2

The third category belongs to products where CO_2 is used as co-substrate i.e. where CO_2 sequestration occurs via natural metabolic pathways to produce commercially important products. The best examples of products in this category are from reductive TCA cycle with

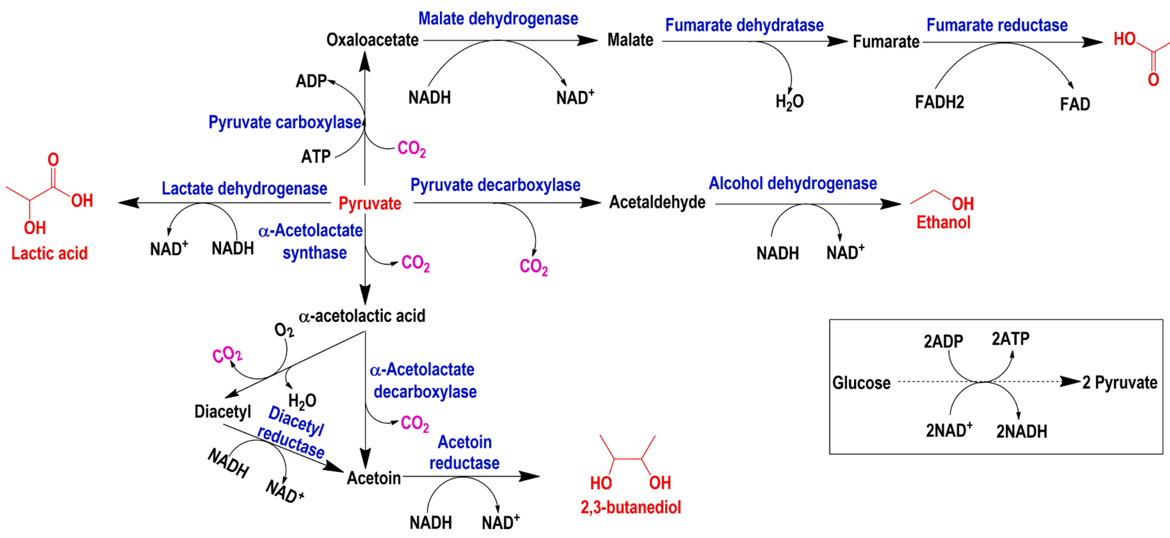

Fig. 1. Metabolic pathways for different biochemicals with CO_2 participating as co-substrate or byproduct [12,26,32].

oxaloacetate (OAA) as precursor, which is formed through carboxylation of C3 metabolites, pyruvate or phosphoenolpyruvate [12]. OAA can be transformed to malic acid, fumaric acid or succinic acid (SA) (Fig. 1). Thus, production of these platform chemicals via biological route can make significant contribution towards decarbonisation.

3. Advantages of biogenic CO_2 from fermentation industry

The global CO_2 market was 230 million tonnes in 2021 and is forecasted to reach 520 million tonnes by the year 2035 [37]. A large fraction of its supply can be fulfilled by using CO_2 coming from fermentative routes, a source of biogenic CO_2 as opposed to CO_2 stemming from fossil resources. Further, the usage of biogenic CO_2 is preferred to ensure that the products remain carbon neutral to contribute toward climate neutrality. For example, every year 69.7 Mt of CO_2 is generated in Europe only from upgradation and combustion of biogas as well as bioethanol and other processes based on fermentative production of chemicals [23]. Presently many technologies are developed, focussing towards direct air capture (DAC) to capture selectively atmospheric CO_2, where its concentration is much lower (424 ppm). The process of capturing atmospheric CO_2 requires more complex and requires energy-intensive methods, making it currently an order of magnitude more expensive than capturing biogenic CO_2 produced during fermentation (Fig. 3).

The cost of purifying one ton of CO_2 released during bioethanol production is significantly lower (6–14 USD) as reported by Bains et al [39], when compared to the capture cost of 200–600 USD per ton of CO_2 from DAC technologies [40]. The lower CO_2 purification cost obtained from bioethanol plants is due to the relatively high concentration of CO_2 released during fermentation process [22]. This high concentration allows for easier and more cost-effective treatment of impurities, utilizing existing gas-to-liquids (GTL) feed purification units. Recently in February 2023, Carbon Recycling International (CRI) commenced their first commercial plant in China, wherein their proprietary Emissions-to-Liquids Technology could valorise CO_2 emitted from industrial plants to methanol. The plant is anticipated to produce 110,000 tonnes/year of low carbon and sustainable methanol [41]. Likewise Carbon Engineering have developed and showcased “Air to Fuels technology” in which they first concentrate CO_2 using DAC technology and in second step they split water to produce hydrogen and oxygen. Further, they have demonstrated the catalytic conversion of CO_2 and H_2 to produce hydrocarbons and a variety of drop-in-fuels [42].

The exit gas stream of various industries also contain CO_2 and it was found that these industrial streams are contaminated with significant amounts of several impurities that require extensive and costly purification methods. Some of the impurities are corrosive and create problems in transport and long-term storage [43]. On the other hand, CO_2 from fermentation industry is of high-quality, with impurities that are easier to eliminate than those of fossil sources. For example, The CO_2 stemming out from bioethanol industry (70-80 Mt on annual basis) require no or very little purification, can be used directly and would bring down the sequestration costs [23,41,42]. Hence, technologies as developed by CRI can easily be coupled with any plants, which produce biogenic CO_2 especially via the fermentation route, which is much purer, compared to flue gases in terms of composition and concentration. Alternately, considering the significant cost difference, CO_2 can be captured from bioethanol plants and valorised to various products such as gasoline, diesel and sustainable aviation jet fuels, offering a more economically feasible and efficient pathway towards reducing CO_2 emissions and achieving decarbonization goals [42,44].

4. Gas fermentation – An effective way of decarbonisation

An attractive preposition for sequestration of CO_2 and any other GHG released during fermentation processes or from other sources, could be its transformation via catalytic and biological routes using gas fermentation (Fig. 2) [45,46]. Gas fermentation allow the use of microbial catalysts to utilize syngas, CO_2, CO, CH_4 as carbon source to manufacture a range of products including platform chemicals, fuels and polymers. Many organisms in nature contain CO_2 fixing autotrophic pathways such as Calvin cycle, reductive TCA cycle, Wood-Jungdahl pathway, 3-hydroxypropionate cycle [5,47]. These organisms can be further engineered to efficient cell factories for turning CO_2 into chemicals and fuels. The CO_2 is an oxidized molecule and can be reduced to a different carbon sink including cell mass, fermentation products and byproducts [48]. The success of gas fermentation also depends on quality and purity of CO_2. The exit gas stream of many industries contains lots of impurities retarding the performance of process. The high-quality CO_2 coming from biological routes with minimal or no inhibitors, can be easily integrated with gas fermentation to obtain these products along with use of energy rich and reduced co-substrate for manufacturing a target product which is more oxidized than this co-substrate. The ability to fix CO_2 increases with enhancement in the electron density of the co-substrate [49,50]. For example, *Cupriavidus necator* (also known as *Ralstonia eutropha*) is a Gram-negative respiratory facultative lithoautotrophic and a metabolically versatile bioproduction platform bacterium. The bacterium is well-known to accumulate the biodegradable PHA from CO_2 and hydrogen as source of electrons and

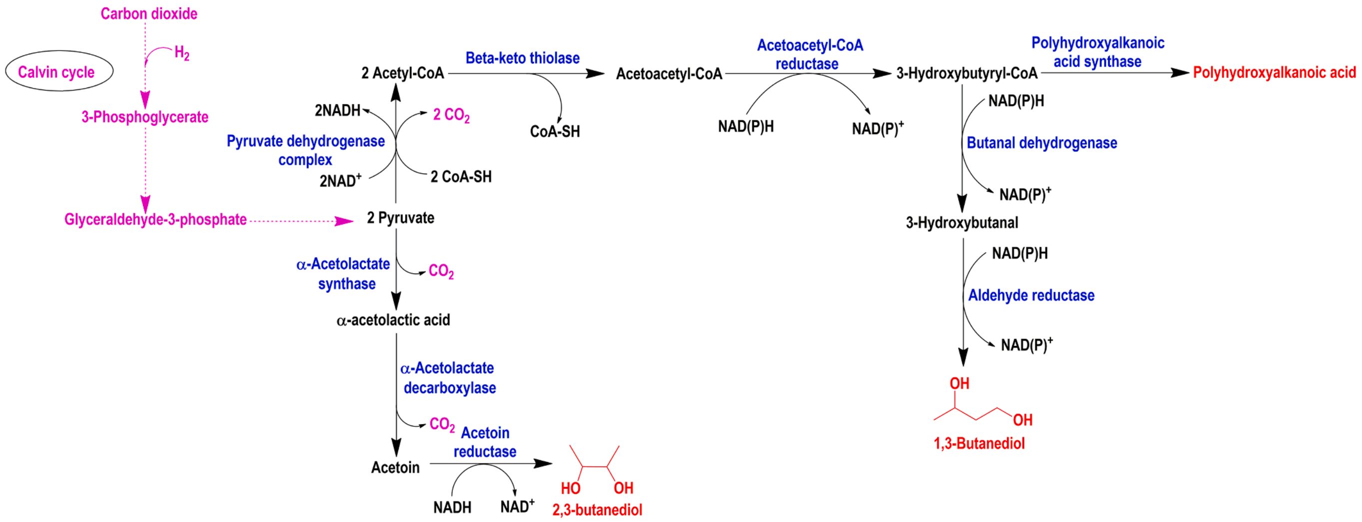

Fig. 2. Biological routes for CO_2 transformation into different metabolic products [26,48,53].

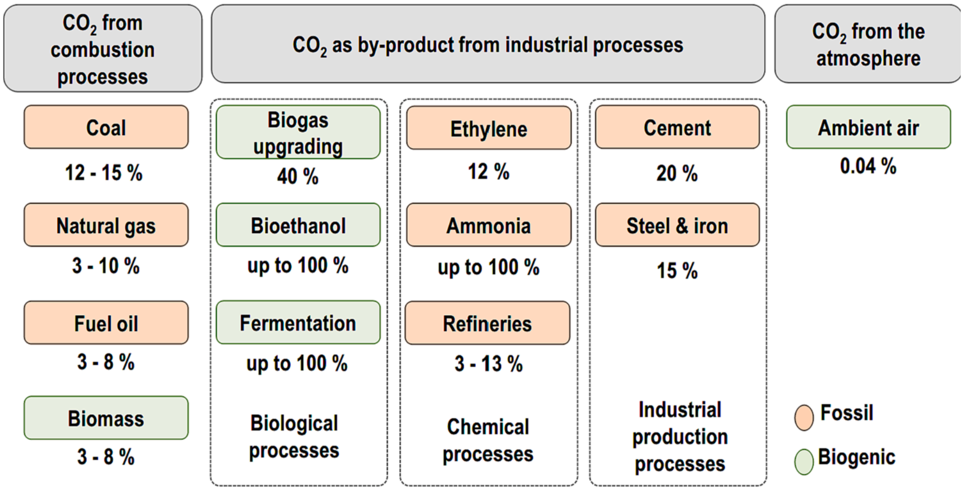

Fig. 3. Comparisons of potential fossil and biogenic CO_2 sources [23,38].

oxygen as electron acceptor [50]. The attenuation of genes responsible for PHA production coupled with nutrient limitation conditions results into pyruvate accumulation which can be channelised towards a variety of products [51]. For example, *C. necator* has been metabolically engineered to produce 1,3-butanediol, 2,3-BDO, 3-HP, isopropanol etc. from CO_2 [48,50,52,53]. Besides gas fermentation, microbial electrosynthesis (MES) is an emerging technology that utilizes microbes to convert CO_2 into chemicals with the help of renewable power generated using wind and solar. In this method, a microbial culture is grown in an electrochemical cell, where a cathode electrode supplies electrons coming from oxidation of water molecules/organic chemicals to the microorganisms for CO_2 reduction into range of products including organic acids (formic, acetic, butyric acid) and alcohols (ethanol, n-butanol) [9]. Leeson et al., have reported that carbon capture and storage (CCS) cost across of the four industries namely iron and steel, oil refining, pulp and paper and cement industry is highly inconsistent and ranges between 20 and 120 USD/tonne CO_2, therefore, an integrated gas fermentation/MES plant next to emission source can present a feasible model to facilitate carbon capture and incentivise these industries [54].

5. Bio-based *vs*. Fossil-based products: From an environmental sustainability viewpoint

The bio-based manufacturing of chemicals is a potential alternative to fossil-based production, which is perhaps the most intensively pursued route to secure production of fuels and chemicals as well as to mitigate CO_2 emissions. Tremendous advances in the area of synthetic biology, omics (genomic, proteomic and metabolomic) technologies and high-throughput screening have enabled biotechnology innovations. Today several unconventional chemicals, which were commercially produced only through petrochemical route, are scaled-up using fermentation route as well. In this regard, even gas fermentation has been strategically exploited for the biomanufacturing of carbon neutral or carbon negative bio-based products, by exploiting the microbes that can metabolize carbon-rich gases such as CO, CO_2 and CH_4 with later two being GHG as well. The subsequent section comparatively assesses the environmental benefits offered by some bio-based productsthat are either commercialized or in the process of commercialization, with petro-based products.

5.1. Ethanol

LanzaTech Technologies revived the commercial interest in acetogens, which are a group of bacteria that can transform C1 feedstocks (CO_2, CO, formate) to acetyl-CoA since they contain Wood–Ljungdahl pathway, also known as reductive acetyl-CoA pathway and contain a signature enzyme complex known as CO dehydrogenase/acetyl CoA synthase. This US-based company industry partnered with Shougang Group Co. Ltd., a leading Chinese iron and steel producer, Tangshan Caofeidian Beijing-Hebei Cooperation Green Industry Investment FUND, Shanghai Dehui Group Co., Ltd., its New Zealand partner, Tang Ming Group (Wellington) Investment Ltd. and Mitsui Co., Ltd. and commercialized their gas fermentation technology for continuous ethanol production from recycled steel mill emissions, at Beijing Shougang LanzaTech New Energy Science & Technology Co. Ltd [55]. This China-based plant is operational since 2018 and has produced 40 million gallons of ethanol, off-setting 2 million Mt CO_2 [56]. This ethanol technology has been proven with refinery off gases and other feedstocks such as municipal solid waste and biomass which are burnt to produce syngas and then valorised to produce ethanol via gas fermentation [57].

5.2. 1,3-propanediol (1,3-PDO)

Earlier, 1,3-PDO was commercially produced through chemo-catalytic route either using acrolein (Degussa-Dupont) or ethylene oxide (Shell route) as the starting feedstock. However, Dupont successfully developed a synthetic pathway in *E. coli* which was able to produce 1, 3-PDO from corn-derived glucose and later commercialized the process, along with Tate & Lyle as their partners [35]. Dupont claims that their commercial process for the manufacturing of glucose-derived Susterra®1,3-propanediol consumes up to 42% less energy and reduces GHG emissions by $>$ 56% compared to chemically derived 1,3-PDO [58].

5.3. Succinic acid

Succinic acid (SA) is yet another platform chemical which is produced commercially via petrochemical route. In last 10 years, several pilot-scale and commercial plants for bio-based SA production have been demonstrated its edge in terms of environmental sustainability. For example, the carbon footprint of commercial bio-based SA which was manufactured by Reverdia (joint venture of DSM and Roquette), under the brand name Biosuccinium® was merely 0.9 kg CO_2e/kg acid compared to 1.9 kg CO_2e/kg acid obtained via petrochemical route [59]. In 2022, Technip Energies acquired this technology for DSM for sustainable polymer synthesis, which used low-pH tolerant proprietary yeast for SA production from glucose [60]. Yet another commercial process developed by Succinity, a joint venture of BASF and Corbion Purac, used a native, but proprietary *Basfia succiniciproducens* which could fix CO_2 through reductive TCA pathway [61]. The company claimed that the carbon footprint of their product Succinity Biobased SA® was 60 % lesser than that of fossil-based SA [62]. Likewise, Bio-Amber who partnered with Mitsui & Company, claimed that their yeast based SA technology had nearly zero carbon footprint [63].

5.4. 1,4-Butanediol (1,4-BDO)

1,4-BDO is yet another industrially important chemical predominantly used in the production of polymers and solvents. It is conventionally manufactured through the Reppe's process that uses formaldehyde and acetylene as feedstocks. However, owing to safety and environmental issues associated with using such feedstocks, alternate commercial technologies were explored for its production [64]. Recently, a cost and techno-competitive biological process was developed by US based company Genomatica, jointly with Tate & Lyle Group for commercial production of 1,4-BDO. Using engineered *E. coli* and taking glucose as starting feedstock, they licensed their technology to Novamont, Italy for its commercial production with 30,000 tonnes capacity in 2016. The life cycle assessment (LCA) study reveals 56 % reduction in GHG emissions from the commercial facility of bio-based 1,4-BDO as compared to petrochemical-based BDO process. The company further exemplifies that if all the 1,4-BDO (~2 million tonnes/ year) is produced using Genomatica' s technology, it can save nearly 7 million tonnes of GHG/ year [65].

5.5. 1,3-Butanediol or 1,3-butylene glycol (1,3-BG)

1,3-BG finds numerous applications in personal, healthcare and cosmetic products. Genomatica developed a sugar-based commercial fermentation process for production of 1,3-BG and presently it is sold under the brand names Brontide^{TM}and Alvea^{TM}. They have shown potential environmental benefits of Brontide^{TM} over fossil-based counterpart and have claimed that its global warming potential is merely 1.86 kg CO_2e compared to 3.78 kg CO_2e by fossil-based 1,3-BG. Since it is also a precursor molecule for the production of butadiene, Versalis has jointly ventured with Genomatica for production of bio-butadiene [66,67].

5.6. 1,3-Butadiene

Invista Nylon Chemicals collaborated with LanzaTech to develop bio-butadiene using gas fermentation [68]. In 2022, they unveiled a dedicated facility in China that will deploy proprietary, 1,3-butadiene-based Adiponitrile (ADN) technology. ADN is an important chemical intermediate for the synthesis of Nylon 66. This technology is claimed to result in 60% and 80% lower GHG emissions compared to propylene and adipic acid based ADN, respectively [69].

5.7. Industrial solvents

Recently, LanzaTech demonstrated continuous production of acetone and isopropanol produced by gas (50% CO, 10% H_2, 20% CO_2 and 20% N_2) fermentation in 120 L pilot-scale fermentor using recombinant strain of acetogenic bacterium *Clostridium autoethanogenum* with productivity and selectively being 3.0 g/L/h and 90%, respectively. LCA study revealed that acetone and isopropanol showed a negative carbon footprint of – 1.78 kg CO_2e/kg and – 1.17 kg CO_2e/kg, respectively [70].

5.8. Aviation fuel

Presently all the commercial flights use the aviation fuel derived from the petrochemical route. However, LanzaTech claims that carbon footprint of its sustainable aviation fuel (SAF) with a brand name LanzaJet is merely 14 and −10 g CO_2e/MJ when the starting feedstocks are biogas and renewable energy respectively, compared to 89 g CO_2e/MJ of fossil equivalent jet fuel [71].

5.9. Polyhydroxyalkanoates

In 2019, Newlight Technologies, a US based company started its fully functional commercial plant "Eagle 3" for the production of polyhydroxybutyrate (PHB) from ocean dwelling natural microbes that use air and GHG including CO_2 as substrates to manufacture carbon negative plastics [72]. PHB is being sold under the brand name Aircarbon^{TM} and its carbon footprint is −88 kg CO_2e/kg, as independently calculated and certified by Carbon Trust. Presently, this regenerative polymer is catering industrial segments such as footwear, and textiles [73]. Likewise, Mango Materials demonstrated the production of pure PHB using methanotrophs, which thrive on waste methane stream (obtained from landfills, biogas, wastewater) in a close-loop system and their product is sold under the brand names YOPP and YOPP+ [72,74]. The company claims that their YOPP fibers degrade within ~ 6 weeks in marine environment.

5.10. Essential amino acids

These are another category of food-grade chemicals, which are produced commercially by microbial fermentation. Lysine, which belongs to the category of essential amino acid, had a market value of 8,472.6 million USD in 2022. Presently, Ajinomoto, Japan holds 16 % of the total global market of lysine [75]. With rising awareness towards environmental sustainability, Evonik, one of the commercial lysine manufacturers is close to achieve carbon neutral fermentation process from corn-derived glucose using *Corynebacterium*, at its manufacturing site in Castro, Brazil. The company claims that only 0.1 kg CO_2 equivalent is generated per kg of BIOLYS®77, which is the trade name for their product containing 77 % ratio of lysine HCl [76].

5.11. Polypropylene and polyethylene

These polymers are conventionally produced via petrochemical route and find numerous applications in diverse sectors like automotive, building and construction, packaging, medical, electrical and electronics etc. Recently in April 2023, Citroniq and Lummus Technologies signed a letter of intent to open a commercial plant for polypropylene production that will annually sequester 1.2 million Mt CO_2 [77]. Citroniq has mastered in its proprietary E_2O process which produces carbon negative plastics and olefins from sustainable feedstocks such as corn. Bioethanol produced from corn is later converted into polypropylene, water with small quantities of by-products using catalytic approach [78]. On the other hand, Lummus Technologies have their Verdene™ technology wherein bioethanol is produced using sustainable feedstocks which is finally converted to bio-polypropylene using a combination of dimerization and olefin conversion technology involving metathesis chemistry [79].

Prior to this development, Braskem, another US giant in petrochemical sector is already producing a range of renewable polymers at commercial-scale under the umbrella brand "I'm green™" at its Brazilian site. When LCA was conducted for its bio-based polyethylene (PE), one kg of finished product imposed a climate change impact of −3.09 kg CO_2e, suggesting that sugarcane-derived renewable PE was carbon negative plastic. Likewise, Braskem's bio-based polymer ethyl vinyl acetate has shown to impose a climate change impact of merely −2.1 kg CO_2e/kg product [80].

All these commercial/pilot-scale bio–based processes and upcoming projects clearly demonstrate that shifting from fossil-based route to fermentative route can incentivise the world in terms of environmental benefits and sustainability. Further, these instances give a strong message that in the near future; hybrid and green technologies are bound to emerge as potent solutions for decarbonizing chemical sector and attaining carbon neutrality.

6. Carbon dioxide removal (CDR) from fermentation as a platform for carbon offsetting

The concept of carbon offsetting as a service involves offering a structured framework that enables hard-to-abate industries to pay for the capture of their CO_2 emissions on a per-ton basis. This service-based approach shifts the responsibility of managing the complete value chain, including CO_2 capture and removal, followed by fixation via storage or utilisation (only for technologies that provide carbon fixation over a prolonged period) to specialised entities equipped with the necessary expertise and infrastructure, assuming the responsibility, along with associated risks and potential financial rewards. The permanent fixation of biogenic CO_2 from fermentation processes can offer a CDR approach and negative emissions technology (NET) for removing CO_2 present in the atmosphere, as biogenic carbon coming from sustainable resources is part of a natural biogenic carbon cycle. Given that fermentation provides one of the most economical routes to produce biogenic CO_2 [23], it can offer a promising platform for the provision of carbon offsetting as a service to hard-to-abate industries.

The key prerequisite for fermentation to be considered as CDR is the permanent fixation of biogenic CO_2. In this context, the CO_2 can be permanently fixed via storage within geological formations, or potentially via routes including permanent retention of carbon, such as building materials. However, it should be emphasised that the latter requires a comprehensive LCA and better understanding of market dynamics to ensure the targeted CO_2 use can offer climate benefits for scalable applications with utilisation of low carbon energy, and displaces a product with poor environmental profile. Therefore, by no means CO_2 use can deliver emissions reduction on the same scale as carbon capture and storage from point sources. Based on the analysis conducted by the International Energy Agency (IEA), it was estimated that while use of CO_2 makes a growing contribution to the reduction of emissions, its contribution in delivering emission reductions is limited to only 13 % of what would be achieved through CO_2 storage alone [81]. However, as European Union is targeting to 5 million tonnes of CDR by 2030, its largest single-site bioethanol plant namely Hungary-based Pannonia Bio, which currently emits 0.5 million tonnes CO_2 aims to permanently store it in depleted natural gas fields and are in talks with potential partners [82].

Estimating the future market of CO_2 use poses significant challenges due to the anticipated reliance on policy frameworks across various applications. It is imperative to ensure that policy and investment decisions concerning the applications of CO_2 are supported thorough LCA offering enhanced understanding and quantification of the climate and environmental benefits associated with these applications. The policy framework should also enable the identification of early market opportunities for scalable and commercially- feasible applications of CO_2 delivering emissions reductions (e.g. CO_2 use in construction and building materials). Moreover, it should enable the establishment of performance-based standards to facilitate the uptake of CO_2-derived options. Although the pathway for fixation of CO_2 via storage is relatively regulated, the near-term scale-up of CO_2 use is hindered by both commercial and regulatory aspects. It is suggested that to promote plant growth, individual markets, such as CO_2 use in building materials, should be potentially increased to at least 10 Mt CO_2 use per annum, close to the current CO_2 demand for food and beverage industries [83]. Sanchez et al. [24] developed a detailed framework which evaluates near-term CO_2 capture opportunities from various biorefineries across United States. They have also proposed that permanent sequestration of biogenic CO_2 can be accomplished either by capturing, compressing and transporting it to potential geological sequestration sites (such as deep saline aquifers) or alternately by using it for enhanced oil recovery (EOR). For instance, the Illinois based corn ethanol plant (1 million tonnes per annum capacity) of Archer Daniels Midland in US is using geological storage as their method for CO_2 storage since 2017. Likewise, ethanol plants of Calgren Renewable Fuels and Bonanza Bioenergy based in California and Kansas are using CO_2 for EOR [84]. However, for the former case, a comprehensive network of pipelines needs to be created for large scale CO_2 transport and sometimes the distance between the geological site and biorefinery location is a limitation, enhancing the overall cost of carbon capture and storage.

Alternately conventional fermentation can be replaced with transformative technologies such precision fermentation. It is yet another powerful and indirect way of reducing carbon footprint significantly, as it uses specialized recombinant microbial cell factories, capable of producing commodity chemicals with high-titre, productivity and yields with minimal or no by-product formation [85]. Precision fermentation is already gaining importance in the food sector wherein microbes are exploited for production of artificial and animal-free protein mimicking characteristics of proteins such as whey, egg and collagen. Recently, Crandell et al. have proposed an emerging and hybrid approach in which gases such as CO_2 and CO can be electrochemically reduced to acetate and then via precision fermentation acetate can be transformed into a variety of sustainable fuels and chemicals [86].

7. Future perspectives and conclusion

Establishing a CO_2 based biorefinery is a fascinating dream as well as long-standing challenge. The CO_2 burden on environment could be reduced through conversion of CO_2, available from different sources, into plethora of value-added products. Photosynthetic biological systems such as cyanobacteria, microalgae, macroalgae etc make use of light, water and CO_2 to produce a range of products such as hydrogen, triacylglycerol, proteins, sugar, starch and all these could be transformed into an array of products via different routes [45]. In this regard, LanzaTech has successfully deployed its gas fermentation technology for producing a number of carbon smart products ranging from monomeric and polymeric materials to fragrances, solvents, chemicals and fuels [87]. Presently its client and partnership list include industrial giants from diverse sectors like Arcelor Mittal Steel Company, Sekisui Chemicals, Suncor Energy, Total Energies, India Glycols Limited, British Airways, Virgin Atlantic, Unilever, L'Oreal, Lululmen, Zara etc [87,88]. Other option could be using the CO_2 from one fermentation process with another one requiring CO_2 as co-substrate such as microbial ethanol and SA production. The purity of CO_2 coming from fermentation industry is high enough to be directly used in the food and beverage sector. The other applications include dry ice, electronics, water purification, refrigerant gas, gaseous fertilizer and food packing agent or for carbonating beverages, pulp and paper, metal industry and welding fire suppression technologies [23].

The CO_2 capturing technologies are well established, but they incur high costs stemming from capture, transportation and storage making it very expensive. On the other hand, direct or indirect use of CO_2 from green sources including fermentation is a strategic approach for reducing the carbon emission. The biological processes such as fermentation, AD etc are clean source of high-quality CO_2 which can be easily channelized towards other purposes without the need for capturing, transportation and storage. Further, biological routes can also be exploited to use CO_2 as main or co-substrate to manufacture a range of products. However, development of biorefineries which could utilize this large volume of CO_2 originating from biogenic sources and biological processes is limited and significant progress need to be made in this direction. With the emerging gas fermentation and MES technology several industrially important organic molecules are produced using CO_2 from carbon intensive industrial sectors using native and genetically modified organisms and renewable electricity. These technologies have potential to replace fossil-based production and revenue generated can offset the operational cost. Authors are optimistic that this article will accelerate the intensive research towards fermentation processes releasing or capturing CO_2 along with better use of released CO_2 and eventually all these will help in cutting down the carbon footprints and creating a carbon neutral society.

CRediT authorship contribution statement

Deepti Agrawal: Writing – original draft, Writing – review & editing. **Kelvin Awani:** Writing – original draft, Writing – review & editing. **Seyed Ali Nabavi:** Writing – original draft, Writing – review & editing. **Venkatesh Balan:** Writing – review & editing. **Mingjie Jin:** Writing – review & editing. **Tejraj M. Aminabhavi:** Writing – review & editing. **Kashyap Kumar Dubey:** Writing – review & editing. **Vinod Kumar:** Conceptualization, Writing – original draft, Writing – review & editing, Project management.

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.

Data availability

Data will be made available on request.

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