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Revising the dark fermentative H_2 research and development scenario – An overview of the recent advances and emerging technological approaches

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ABSTRACT

The indiscriminate use of fossil fuels has led to several challenges such as greenhouse gas emissions, environmental degradation, and energy security. Establishment of clean fuels is at the forefront of science and innovation in today's society to curb these problems. Dark fermentation (DF) is widely regarded as the most promising clean energy technology of the 21st century due to its desirable properties such as high energy content, its non-polluting features, its ability to use a broad spectrum of feedstocks and inoculum sources, as well as its ability to use mild fermentation conditions. In developing nations, this technology could be instrumental in establishing effective waste disposal systems while boosting the production of clean fuels. However, DF is still hindered by the low yields which stagnate its commercialization. This paper reviews the recent and emerging technologies that are gaining prominence in DF based on information that has been gathered from recent scientific publications. Herein, novel enhancement methods such as cell immobilization, nanotechnology, mathematical optimization tools, and technologies for biogas upgrading using renewable H_2 are comprehensively discussed. Furthermore, a section which discusses the potential of bioenergy in Sub-Saharan Africa including South Africa is included. Finally, scientific areas that need further research and development in DF process are also presented.

1. Introduction

The growing concerns about the anthropogenic CO_2 emissions and depletion of natural resources have resulted in an enormous search for sustainable energy resources [1–3]. Therefore, a wide variety of clean technologies are being investigated [4,5]. Hydrogen (H_2) is seen as one of the most appealing energy resources as a result of its qualities such as high energy content (120 kJ g^{-1}), its production using various techniques (e.g. steam reforming, gasification, water electrolysis and fermentation), its carbon-sequestration abilities during downstream processing, and its diverse industrial applications [6–10].

Hydrogen is expected to play a pivotal role in decarbonising the energy and transport sector [11]. The potential of a H_2-driven economy is already being recognized in several countries. For example, a total of 8000 fuel cell vehicles are now registered with the International Energy Agency, of which 4500 vehicles are coming from the United States and another 2500 vehicles from Japan [12]. It is estimated that more than 10 000 H_2 fuel cell-powered forklifts are already in use in several

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warehouses in the United States [13]. Furthermore, 192 fuel cell vehicles are currently running under demonstration projects in Europe and it is anticipated that around 350 000 vehicles will be sold to the general public by 2020 [14]. Technology roadmaps for H_2 and fuel cells have been established already in countries like Japan, China and the United States, to accelerate the industrialization of H_2 related technologies [15]. According to recent reports, the global H_2 market was estimated at 129 billion US dollars in 2017 and is expected to increase to 183 billion US dollars by 2023 [16].

Currently, steam reforming and gasification of fossil-derived fuels are still considered the primary sources of H_2 worldwide [11]. However, these processes undermine the purpose of using H_2 as a clean technology, as more CO_2 is emitted during the processing of fossil fuels [17,18]. It is therefore vital for a H_2 driven-economy to make environmental and economic sense [19]. Hydrogen from waste biomass represents an economical and environmentally-friendly approach because this process uses diverse feedstocks [20–23]. Amongst the H_2 bioprocesses, DF is considered as the most promising clean technology of the 21st century because it can valorise diverse feedstocks including waste materials under mild fermentation conditions [24–26]. However, the establishment of a large-scale DF process has not yet been realized due to the incomplete conversion of feedstocks that results in low yields [27]. Therefore, this calls for the implementation of robust technologies which will fast-track the development of this process.

In recent years, there has been a surge in biofuel development initiatives in Sub-Saharan African countries with the aim of boosting economic growth, energy security, and rural development within the region [28]. The development of clean energy is fuelled by several factors such as high availability of non-arable land, abundance in biomass resources, and warm climate [28]. Biofuels such as bioethanol and biodiesel are being explored in many Sub-Saharan African nations, and it is hoped that these initiatives will lead to their commercialization [4]. DF is also receiving significant attention due to its socio-economic benefits, and the fact that this process can be incorporated into a biorefinery concept.

As the body of knowledge is constantly expanding in DF, it is imperative to update the scientific community with novel and emerging technologies that can fast-track the advancement of this technology. This article examines the novel technologies that are gaining prominence in DF based on recent scientific publications. Biogenic H_2 enhancement methods such as cell immobilization, nanotechnology, mathematical optimization tools, and biogas upgrading, are reviewed in this article. A section that highlights the potential of biofuels in Sub-Saharan Africa including South Africa is included. Finally, conclusions and suggestions for further research in DF, particularly from organic wastes, are provided.

2. An overview of the process barriers facing the DF process

Despite the efforts that have been undertaken over the past decade,

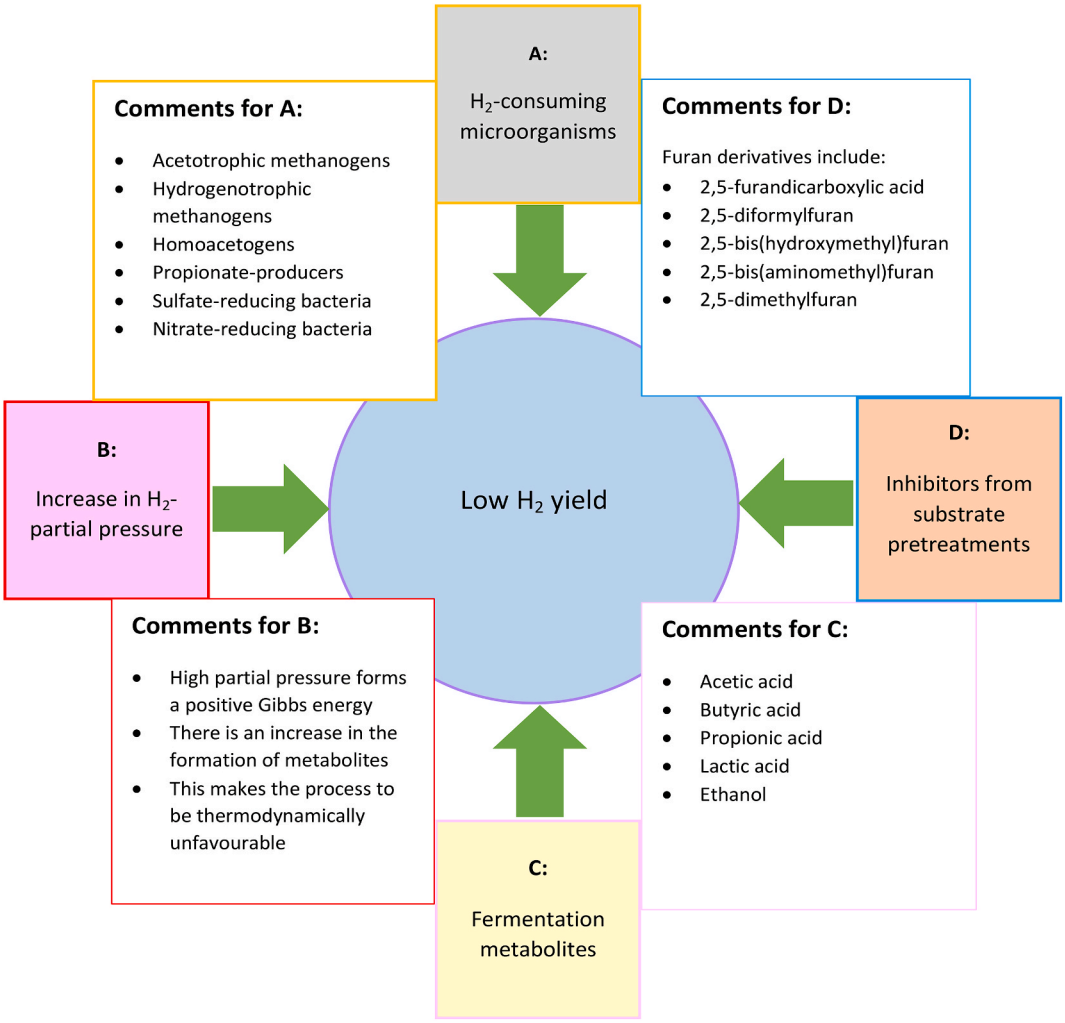

Fig. 1. An overview of the process barriers facing the DF process. Adapted and modified from Sekoai et al. [10]. Letters A, B, C and D represent the different process barriers contributing to the low H_2 yields.

DF is still hindered by low yields which delay its industrialization (Fig. 1). The substrates are partially converted into H_2 and remain in the medium in the form of volatile fatty acids (acetic acid, butyric acid, propionic acid, etc.) and alcohols (butanol, ethanol, propanol, etc.) [29–31]. These by-products shift the reactions from acidogenesis to solventogenesis, resulting in low H_2 yields [32–35]. Theoretically, 4 mol H_2 mol^{-1} glucose is produced from the acetic acid pathway while 2 mol H_2 mol^{-1} glucose is synthesized from the butyric acid pathway as shown in Equations (1) and (2), respectively. Currently, 1–3 mol H_2 mol^{-1} glucose is reported in the literature and 60–70% of substrate is not used even under optimum bioprocess conditions [36,37].

DF studies use various microorganisms that are classified as pure-cultures or mixed-cultures [38,39]. Clostridial strains are the main H_2-producing species and can generate up to 3 mol H_2 mol^{-1} glucose [40,41]. However, these microorganisms will not be suitable for scale-up processes because they require stringent aseptic conditions and this is impractical in industrial fermentation systems [42–46]. Moreover, some *Clostridium* sp. such as *C. articum* and *C. barkeri* are not favoured in DF because they use H_2 to produce undesirable compounds such as propionic acid i.e. Equation (3) and lactic acid i.e. Equation (4) [47–49]. Other clostridial species co-produce H_2 and ethanol, causing low H_2 yields i.e. Equation (5) [50,51].

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (1)$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \quad (2)$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \quad (3)$$

$$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH + 2CO_2 \quad (4)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2OH + H_2O + CH_3COOH + 2CO_2 + 2H_2 \quad (5)$$

As a result, most DF studies use mixed-cultures due to the following reasons: (i) no sterilization is required, (ii) they consist of various biofilm-forming bacteria, (iii) there is a synergism between bacteria, and (iv) they use diverse feedstocks [52–54]. However, the use of mixed-cultures has been argued in DF as well. Mixed-culture consists of non H_2-producers such as acetotrophic and hydrogenotrophic methanogens, sulfate-reducing bacteria, nitrate-reducing bacteria, homoacetogens, iron-reducing bacteria, lactic acid bacteria, etc. [55,56]. Although various pre-treatment methods are used to inhibit these microorganisms, they still thrive during the DF process and compete with H_2-producers [57,58]. This implies that robust bioprocess technologies are needed to address these issues.

3. Recent advances and emerging technologies in DF process

3.1. Cell immobilization

Studies are now using cell immobilization to improve the H_2 yields and also minimize the accumulation of inhibitors during DF [59,60]. This approach favours the DF systems by: (i) maintaining high cell concentrations; (ii) stabilizing the fermentation pH; (iii) resisting the effect of H_2-consumers; (iv) enabling an easier downstream process; and (v) allowing the reusability of cells [61,62]. Immobilization methods involves adsorption, entrapment, encapsulation, cross-linking, and covalent binding [63,64]. Moreover, various support materials are used to immobilize the acidogenic microorganisms [65,66], and these carriers are selected based on their internal geometry, mechanical stability, pore size, specific surface area, and thermal stability [67,68]. Matrices such as inorganic materials, carbon-based materials, natural polymers, and synthetic polymers are used to encapsulate the H_2-producers [69,70]. Amongst these, natural polymers such as agarose, alginate, cellulose, collagen, and keratins are widely used due to their high accessibility, biocompatibility, non-toxicity, cost-competitiveness, and large-surface-area [71]. Nevertheless, natural carriers suffer from low mechanical stability but this is circumvented by binding them to stabilizing materials such as polyvinyl chloride, polyvinyl alcohol, inorganic mesoporous silica, activated carbon, ethylene glycol, metals, etc. [72,73]. Immobilized biocatalysts are used in the enhancement of H_2 yields. Zhang et al. [74] obtained an optimum H_2 yield of 1.203 mol H_2/mol glucose using immobilized co-cultures of *Enterobacter cancerogeous* and *Enterobacter homaechei*. Furthermore, a 259% increase in H_2 yield was achieved using immobilized biocatalysts [74]. Han et al. [75] studied the effect of packing ratio (inoculum fraction of 10–20%) and substrate loading rate (8–40 kg L^{-1} d^{-1}) on DF process using an immobilized reactor. Herein, a maximum H_2 production rate of 353.9 mL H_2 L^{-1} h^{-1} was achieved at a packing ratio of 15% and substrate loading rate of 40 kg L^{-1} d^{-1}. In another study, a *Clostridium* sp. T2 strain was immobilized with mycelial pellets in the bioaugmentation of H_2 yield using corn-stalk hydrolysate. The immobilized biocatalyst produced a maximum H_2 yield of 0.0142 mol H_2 L^{-1} h^{-1} at an optimized hydraulic retention time (HRT) of 6 h and substrate concentration of 20 g L^{-1} [76]. This yield was 2.6 times higher than that of suspended mycelial pellets [76]. Recently, three porous particulate carriers such as activated carbon, bagasse and brick were evaluated in the encapsulation of *Clostridium acetobutylicum* for production of H_2 [77]. The use of entrapped biocatalysts increased the concentration of cells within the medium, resulting in high glucose consumption [77]. In another recent study, immobilized mutated (with ethidium bromide and ultraviolet) co-cultures of *Rhodobacter* M19 and *Enterobacter aerogenes* were studied in DF using brewery effluent [78]. An optimal H_2 yield of 2877 mL H_2 was achieved using immobilized ethidium bromide-mutated co-cultures [78]. The immobilized ethidium bromide-mutated co-cultures also enhanced the COD removal by 85% [78]. Furthermore, it has been shown that cell immobilization improves the activity of the predominant H_2-producers such as *Clostridium*, *Bacillus*, and *Enterobacter* species [79–82]. In addition to these studies, a wide variety of support materials have been used in recent years for the immobilization of DF biocatalysts as shown in Table 1.

3.2. Nanotechnology

The field of nanotechnology is receiving increasing prominence in DF due to the intrinsic properties of nanoparticles [99–102] which enables them to be used in diverse areas such as engineering, medicine, agriculture, food industry, electronics, material sciences, etc. [103–108]. These materials have outstanding properties such as large-surface-area, high adsorption capacity, high catalytic efficiency, and high reactivity [109–111]. The mechanisms surrounding the effect of nanoparticles on DF are not well elucidated in the literature. But studies have suggested that these nano-based additives provide a large-surface-area for bacteria to attach to these materials, thereby catalysing the H_2-producing reactions [112–114]. They also stimulate the H_2-producing enzymes ([Fe–Fe]- and [Ni–Fe]-hydrogenase) and electron-transfer proteins (ferredoxins) [114,115]. Therefore, different nanoparticles such as metallic nanoparticles (Ni, Ag, Fe, Cu, Pd, and Au), metal oxide nanoparticles (MgO, TiO_2, NiO, Fe_2O_3, CuO, ZnO, and $NiCo_2O_4$), nanocomposites (Si@$CoFe_2O_4$ and Fe_3O_4/alginate), and graphene-based nanomaterials are used in the enrichment of H_2 of yields [114,116,117].

Metallic nanoparticles are applied in numerous fields due to their remarkable features such as high catalytic, electrical, optical and magnetic behaviour, chemical and mechanical stability, and large-surface-area [118–123]. Examples of metallic nanoparticles include iron (Fe), copper (Cu), gold (Au), silver (Ag), palladium (Pd), zinc (Zn), cobalt (Co), and Nickel (Ni) [112,124–126]. Kodhaiyolii et al. [127] developed bimetallic nanoparticles (Co–Ni) for co-production of H_2 and bioethanol using *Citrobacter fruendii*. These nanomaterials produced low H_2 but enhanced the production of ethanol [127]. This is because *Citrobacter fruendii* is not a potent H_2-producer in comparison to *Clostridium* sp. [10,128–130]. However, Zhang and Shen [114] enhanced H_2 yield by 46% using Au nanoparticles. The pH of the fermentation medium was also maintained within 6.0–7.0 [114]. In another study, Kalathil et al. [131]

Table 1
Dark fermentative H_2 production using various immobilization materials.

Support material	Inoculum	Substrate	Temp (°C)	pH	Evaluation of H_2 production process	H_2 yield	Reference
Activated carbon	*Enterobacter Enterobacter homaechei 83*	Molasses	37	–	Cell immobilization enhanced the H_2 yield by 259%.	1.203[a]	[74]
Alginate + AC	Mixed cultures	Fruit waste	36	7.0	Co-immobilization improved the production of H_2.	0.029[a]	[83]
Alginate + AC	Mixed cultures	Synthetic medium	37.5	6.0	Complete substrate utilization was achieved in the immobilized process.	–	[84]
PSSP + WM	Mixed bacteria	Wheat starch	37	7.0	H_2 increased by 2.1 times when the HRT was reduced from 5 to 1 day.	2.1[a]	[85]
Coconut coir + PVC tubes	*Bacillus amyloliquefaciens* CD16 *Bacillus thuringiensis* EGU45	Domestic waste Industrial effluent	37	7.0	H_2 was increased by 4- to 10- folds and 3- to 5- folds, respectively.	100–120[b]	[86]
Coconut coir + PVC tubes	*Bacillus amyloliquefaciens* CD16	Industrial effluent	37	7.0	The H_2 yield was 1.18 times higher in the immobilized process.	165[c]	[87]
Mutag BioChip™	Mixed bacteria	Synthetic medium	37	5.5	There was low acetate-to-butyrate ratio during H_2 production.	1.80[a]	[79]
Brick	*Clostridium acetobutylicum*	Synthetic medium	37	6.5	There was a high of conc. of bacterial concentration during the process.	1.81[a]	[77]
PVDF membrane	*Rhodobacter* M 19	Brewery effluent	37	6.9	The highest H_2 was produced using EtBr mutated immobilized co-cultures.	2877[d]	[78]
	Enterobacter aerogenes				The immobilized co-cultures achieved a high COD removal of 85%.		
Polyurethane foams	*Enterobacter aerogenes*	Synthetic medium	37	–	Immobilized cells were repeatedly used in batch and continuous processes.	0.6[a]	[88]
Corn stalk	*Bacillus cereus* A1		37	6.5	A two-step continuous H_2 production process was developed.	1.81[a]	[89]
	Brevundimonas naejangsanensis B1				Immobilized bacteria could hydrolyse starch directly.		
Polyester fiber	Mixed bacteria	Wheat waste	39–55	5.5–6	Optimum H_2 was produced at: PN = 240, SC = 10 g L^{-1}, and T = 44.9 °C.	2.59[a]	[90]
					RSM proved to be a helpful tool for predicting the optimum variables.	–	[91]
Polyethylene	Mixed bacteria	Synthetic medium	37	5.5	Polyethylene and expanded clay favoured the H_2-producing bacterial groups.		
Polyurethane					Polyethylene and expanded also stabilized the process pH (5.0–4.5).		
Activated carbon							
Expanded clay							
Activated carbon	Mixed bacteria	Synthetic medium	60	6.0	The presence of immobilized cells enriched the conc. of biomass in FBR.	2.2[a]	[92]
					Clostridium was amongst the dominant H_2-producing bacteria in FBR.		
Bamboo stems	Mixed bacteria	Cassava wastewater	36	6.0	The highest H_2 was obtained at OLR of 35 g L^{-1} d^{-1}.	1.1[e]	[93]
					Butyric acid was the most prevalent metabolite.		
Loofah sponge + AC	*Clostridium sporogenes*	Pineapple biomass	33	7.0	Loofah sponge showed a better H_2-producing performance.	0.0359[f]	[94]
	Enterobacter aerogenes						
Porous foam SiC ceramic	Mixed bacteria	Synthetic medium	33	8.0	Sic ceramic resulted in quick start-up period (~5 days) and high H_2 yield.	5.24[e]	[95]
Alginate + PEI	Mixed bacteria	Brewery wastewater	37	7.0	The immobilized cells enhanced the H_2 production rate.	100–600[g]	[96]
Carbon fiber	*Enterobacter aerogenes*	Synthetic medium	30	7.0	The H_2 yield was higher than that of other support materials (PAC and GAC).	2.56[a]	[97]
Carbon cloth	*Enterobacter aerogenes*	Synthetic medium	37	6.0	H_2 production was enhanced by using the conductive carbon cloth.	228.5[h]	[98]

-: Not available, AC: activated carbon, Conc.: concentration, COD: chemical oxygen demand, EtBr: ethidium bromide, FBR: fluidized bed reactor, GAC: granular activated carbon, HRT: hydraulic retention time, OLR: organic loading rate, PAC: powdered activated carbon, PEI: polyethyleneimine, PN: particle number, PSSP: plastic scouring sponge pad, PVC: polyvinyl chloride, PVDF: polyvinylidene difluoride, SC: substrate concentration, Temp: temperature, WM: metal mesh, RSM: response surface methodology, [a]mol H_2/mol glucose, [b]L H_2 L^{-1} feed, [c]L H_2/L crude glycerol, [d]mL H_2, [e]L H_2 L^{-1} d^{-1}, [f]mol H_2 h^{-1} L^{-1}, [g]mL H_2 d^{-1}, [h]mL H_2 g^{-1} glucose.

reported that Au nanoparticles can be used in a microbial fuel cell reactor for co-production of bioelectricity and H_2. Gold nanoparticles stimulate the DF process by enhancing the enzymatic activities, reaction rates, and conversion of substrates [114,131].

Silver nanoparticles are also used in DF due to their superior catalytical, electrical, physical, biological, and chemical characteristics [132–140]. Zhao et al. [112] used Ag nanoparticles at varying concentrations (0–2x10^{-7} mol L^{-1}) in H_2-producing reactors to boost the DF process. A maximum H_2 yield of 2.48 mol H_2/mol glucose was achieved at Au nanoparticles of 20 nm L^{-1}. This yield was 67% higher than that of the control experiment. Elsewhere, it was shown that low concentrations of Ag nanoparticles promote the growth of acidogenic bacteria [138]. Therefore, these results clearly show that Ag nanoparticles have stimulatory effects on H_2-producers, but this is possible at low concentrations.

Other types of metallic nanoparticles are also applied in DF. Beckers et al. [139] studied the effects of Pd, Ag and Cu nanoparticles alongside metal oxide (FeO) nanoparticles on DF using *Clostridium butyricum*. These nanomaterials were attached to porous silica (SiO_2) at low concentration (10^{-6} mol L^{-1}). The cultures that were entrapped on FeO maximized the H_2 yield by 38% when compared to the control tests. This increase was attributed to the enhanced enzymatic activity and electrons

transfer [139]. Mohanraj et al. [115] synthesized Pd nanoparticles using *Coriandrum sativum* leaf extract and studied their effects on H_2 production using *Enterobacter cloacae* and mixed-consortia. A maximum H_2 yield of 1.48 and 2.48 mol H_2/mol glucose was obtained using *E. cloacae* and mixed-consortia, respectively. These values were 0.6% and 6.4% higher than that of the control tests. Mullai et al. [141] reported a H_2 increase of 22.71% using Ni nanoparticles in a DF process from thermally pretreated anaerobic sludge.

Similarly, Sun et al. [142] studied the synergistic effects of Ni nanoparticles and biochar on the DF process. A remarkable H_2 increase of 48% was achieved at the end of the DF process. These additives also reduced the formation of inhibitory metabolites [142]. Biochar consists of various organic and inorganic constituents which stimulate the activity of H_2-producers, improves the buffering capacity of the medium, and enhance the transfer of electrons [7,143]. Whereas Ni nanoparticles stimulate the activity of H_2-producing enzymes because Ni along with Fe ions forms part of the [Ni–Fe]-hydrogenases [130,144]. Iron nanoparticles have also been used in DF studies. These nano-additives enrich the predominant H_2-producers such as *Clostridium* species [113], stimulate the hydrogenase activity [145], reduce the formation of inhibitors [126], improve the buffering capacity [146], increase the transfer of electrons [113], and enhance the utilization of substrate [113]. The metallic nanoparticles that have been used in the enrichment of DF processes are summarized in Table 2.

Metal oxide nanoparticles are also used in many fields due to their unique properties [147–152]. These nanomaterials improve the acidogenic yields by stimulating the activity of H_2-producing enzymes as well as by increasing the substrate conversion efficiency [153,154]. The effects of three metal oxides nanoparticles (α-Fe_2O_3, NiO, and ZnO) was recently evaluated on DF using industrial wastewater [155]. These nanoparticles promoted the activity of H_2-producing pathways such as those of alcohol dehydrogenase, aldehyde dehydrogenase, and hydrogenase. The production of H_2 was maximized by 8–14% when dual (α-Fe_2O_3 + NiO, α-Fe_2O_3 + ZnO, and NiO + ZnO) and multi-nanoparticles (α-Fe_2O_3 + NiO + ZnO) were used in this process, and this favoured the growth of *Clostridium* species [155].

The influence of TiO and Fe_2O_3 nanoparticles on DF using *Clostridium pasteurianum* at various concentration (0–0.8 g L^{-1}) was also evaluated [156]. The use of hematite nanoparticles increased the H_2 production by 24.9% and also maximized the COD removal by 15.4–22.8% [156]. Likewise, Engliman et al. [157] studied the effects of pH and metal oxides (NiO and α-Fe_2O_3) nanoparticle concentrations (0–0.5 g L^{-1}) on thermophilic DF using mixed-consortia. These nano-carriers increased the H_2 yield by 34.38% and 5.47%, respectively, at operational pH of 5.5, and favoured the acetate pathway [157].

Furthermore, mesoporous silica (SiO_2) nanoparticles exhibit outstanding features such as tunable pore size, high chemical and thermal stability, high adsorption capacity, excellent biocompatibility, and large- surface-area [158–162]. These nanomaterials have been used in the enrichment of DF processes by Venkata Mohan et al. [163] and Seifert et al. [164]. The authors reported a remarkable H_2 increase of 544% and 50%, respectively [163,164]. Interestingly, the SBA-15 nanomaterials generated a H_2 yield that was 347% higher than that of activated carbon [163]. Table 2 summarizes the metal oxide nanoparticles that have been used in the optimization of H_2 yield in DF process.

Novel methods are used to impregnate various nanoparticles to produce multifunctional nanocomposites with high chemical and mechanical stability, excellent catalytic and optical properties, and high permeability [165,166]. The synergistic effects of these nanoparticles have been studied on DF, as shown in Table 2. In one of such studies, the influence of Ni-graphene (Ni-Gr) nanocomposites on DF was examined by Elreedy et al. [117] using industrial wastewater. The Ni-Gr nanoparticles (0.06 g L^{-1}) produced a H_2 yield (41.28 mL H_2/g COD) that was 105% higher than that of the control experiments. These nanoparticles also enhanced the H_2 yield by 67% in comparison to the Ni nanoparticles [117]. The interactive effects of iron oxide (Fe_3O_4) nanoparticles and silica (SiO_2) nanoparticles on DF was assessed as well [163]. The newly synthesized Fe_3O_4@SiO_2 nanoparticles were able to function under a broad pH range, possessed high thermal and chemical stability, and high catalytic performance [163]. Furthermore, the co-addiction of hematite (Fe_3O_4) and NiO nanoparticles improved the H_2 yield by 27% during DF [167]. Meanwhile, a 24% increase in H_2 was obtained using sole hematite as additives [167]. This increase was caused by enhanced substrate recovery and ferredoxin-oxidoreductase activity [167].

In addition to metal ions and metal oxides, metal ion salts like $FeSO_4$, $FeCl_2$, $NiSO_4$, $NiCl_2$, and $MgCl_2$ are also used as catalytic agents in DF (Table 2). These studies used a wide variety of inoculums and substrates at different parameters (Table 2). The enhancement effects of these additives are mainly derived from Ni, Fe, Mg, and Ca ions. Ni and Fe ions are well known for their catalytic activity in hydrogenases because they are the main components in these enzymes as mentioned earlier. On the other hand, Mg plays a crucial role in the metabolic activities of H_2-producers [168]. It forms chelates with important intracellular molecules such as ATP and cytochromes [169,170]. Whereas Ca ions serve as entrapment compounds for enhancing the digestibility of feedstocks [171,172].

It is therefore evident from these studies that nanoparticles have desirable effects on DF processes and these materials could play a crucial role in the advancement of this technology. However, these studies are carried out under laboratory-scale conditions and this may not be a true representation of the process behaviour due to the complexities of industrial processes. Therefore, more studies should be conducted at large-scale to gain deeper insights into the effects of these nano-additives on the overall performance of the DF process.

3.3. Mathematical tools

Mathematical-based models are also used in DF due to their ability to provide insights about the effects (individual and interactive) of operating variables on H_2 yields. Application of mathematical tools to develop empirical models to explain the parametric effects of the operating variables could be instrumental in reducing the operational costs in DF by focusing on the most important variables for further optimization. It is noteworthy to mention that statistical approaches employed to develop empirical models used in understanding the parametric effect of operating variables include data-based modelling approach such as response surface methodology (RSM), Artificial Neural Network (ANN), etc. During the experimental collection of data employed in model development, common design of experiments (DoE) such as Box-Behnken Design (BBD), Central Composite Design (CCD), Plackett-Burman Design (PBD), Full Factorial Design (FFD), and Mixture Design (MD) are used. In addition, the use of computational fluid dynamics (CFD) has been shown to be helpful in gaining insights into the prevailing hydrodynamics during DF. It is noteworthy to highlight that there are other existing tools, but these are scantily reported in DF studies.

Amongst these data-based modelling approaches, RSM is a promising tool that is used to investigate the parametric effect of operating variables on H_2 yield, and consequently optimize the H_2 yields [207–210]. RSM is an empirical model-building approach that employs mathematical and statistical techniques [209,211]. The process response (output variable) is influenced by several independent variables (input variables). Additionally, RSM models provide crucial information about the linear and synergistic effects of process variables on the overall H_2 performance [211]. Previous studies relied mainly on the use of traditional techniques such as one-variable-at-a-time (OVAT), but these methods not reliable because they overlook the interaction amongst process variables, and are time-consuming as well [212]. Therefore, RSM (through which second-order polynomial models are developed in most cases) is applied in DF because it considers the effect of interaction among the process variables alongside the main effect of each variable

Table 2
The various types of nanoparticles that have been used in the enhancement of dark fermentative H_2 yields.

Category	Substrate	Nanoparticles	Inoculum source	Operational parameters			H_2 yield	Reference
				Concentration	pH	Temp (°C)		
Metals	Synthetic medium	Ag	Anaerobic cultures	2×10^{-8} mol L^{-1}	8.0–9.4	35	2.48[b]	[112]
	Sodium acetate	Au	Anaerobic sludge	5×10^{-4} mol m^{-3}	4.0	30	105 mL H_2 L^{-1} d^{-1}	[124]
	Artificial wastewater	Au	Anaerobic cultures	–	7.0	35	4.48[b]	[[114]
	Synthetic medium	Cu	*Clostridium acetobutylicum* NCIM 2337	2.5[a]	6.0	37	1.73[b]	[125]
	Synthetic medium	Cu	*Enterobacter cloacae* 811101	2.5[a]	7.0	37	1.43[b]	[125]
	Synthetic medium	Fe	Anaerobic sludge	25[a]	5.5	37	551 mL H_2 g^{-1} VS	[126]
	Synthetic medium	Fe	*Enterobacter cloacae* DH-89	100[a]	7.0	37	1.9[b]	[173]
	Synthetic medium	Fe	Anaerobic consortia	400[a]	7.0	30	1.33[b]	[174]
	Water hyacinth	Fe	Mixed cultures + *Clostridium butyricum* TISTR 1032	250[a]	7.0	35	57[c]	[175]
	Dewatered sludge	Fe	Anaerobic consortia	0.2 g	7.82–8.35	37	30.51[c]	[176]
	Malate	Fe	*Rhodobacter sphaeroides* NNBL-02 + *E. coli* NMBL-04	312[a]	5.6	32	3.1[k]	[177]
	Synthetic medium	Fe	Mixed cultures	50[a]	5.5	60	1.92[b]	[157]
	Grass	Fe	Mixed consortia	400[a]	7.0	37	50.6 mL H_2 g^{-1} dry grass	[178]
	Sugarcane bagasse	Fe	Mixed consortia	200[a]	5.0	30	0.874[b]	[179]
	Synthetic medium	Ni	Anaerobic sludge	50[a]	5.5	37	680[c]	[126]
	Synthetic medium	Ni	Anaerobic sludge	5.67[a]	5.6	33	2.54[b]	[141]
	Industrial wastewater	Ni	Anaerobic consortia	60[a]	6.72	55	24.73[d]	[117]
	Synthetic medium	Pd	*Enterobacter cloacae* 811101	5.0[a]	7.0	37	1.39[b]	[115]
	Synthetic medium	Pd	Mixed cultures	5.0[a]	7.0	37	2.11[b]	[115]
Metal oxides	Distillery wastewater	NiO	Anaerobic sludge	5[a]	5.5	37	0.00673[e]	[180]
	Dairy wastewater	NiO	Anaerobic sludge	10[a]	5.5	37	0.0157[e]	[167]
	Palm oil mill effluent	NiO	*Bacillus anthracis*	1.5[a]	5.5	37	0.563[f]	[181]
	Palm oil mill effluent	CoO	*Bacillus anthracis*	1.0[a]	5.5	37	0.487[f]	[181]
	Wastewater	SiO_2	Mixed consortia	120[a]	5.5	28	7.29 mol H_2 kg^{-1} COD	[163]
	Synthetic medium	SiO_2	Anaerobic sludge	200[a]	5.5	36	1360 L H_2 L^{-1}	[164]
	Peptone yeast broth	TiO_2	*Clostridium pasteurianum* CH5	0.8 g L^{-1}	7.0	35	2.1[g]	[156]
	Synthetic medium	Fe_2O_3	*Clostridium acetobutylicum* NCIM 2337	175[a]	6.0	37	2.33[b]	[182]
	Peptone yeast broth	Fe_2O_3	*Clostridium pasteurianum* CH5	0.8 g L^{-1}	7.0	35	0.0022[e]	[156]
	Cassava starch	Fe_2O_3	*Enterobacter aerogenes* ATCC13408	200[a]	6.0	37	192.4 mL H_2 g^{-1} starch	[183]
	Synthetic medium	Fe_2O_3	*Enterobacter cloacae* 811101	25[a]	7.0	37	1.7[b]	[184]
	Synthetic medium	Fe_2O_3	Mixed cultures	200[a]	6.0	35	3.57[h]	[185]
	Synthetic medium	Fe_2O_3	Mixed cultures	400[a]	7.0	37	1.53[b]	[116]
	Starch wastewater	Fe_2O_3	Anaerobic sludge	25×10^{-3} g	6.8	30	66.22[c]	[186]
	Inorganic salts	Fe_2O_3	Mixed consortia	200[a]	6.0	35	3.57[h]	[185]
	Synthetic medium	Fe_3O_4	Mixed cultures	200[a]	6.6	37	218.63[b]	[187]
	Sucrose wastewater	Fe_3O_4	Anaerobic consortia	2 × 104a	5.5	35	0.39 L H_2 g^{-1} sucrose	[188]
	Synthetic medium	Fe_3O_4	*Clostridium beijerinckii* NCIMB 8052	300[a]	7.0	35	2.1[b]	[189]
		Fe_3O_4	*Clostridium butyricum* CWBI1009	10^{-6} mol L^{-1}	7.6	30	2.1[b]	[139]

(*continued on next page*)

Table 2 (*continued*)

Category	Substrate	Nanoparticles	Inoculum source	Operational parameters			H_2 yield	Reference
				Concentration	pH	Temp (°C)		
	Synthetic medium							
Composites	Industrial wastewater	Ni + Gr	Mixed cultures	60[a]	7.0	55	41.28[c]	[117]
	Dairy wastewater	Ni + Fe_3O_4	Mixed consortia	10[a] and 50[a]	5.5	37	17.2[d]	[167]
	Glucose	C + Fe_2O_3	Mixed consortia	200[a]	6.6	37	218.63[i]	[187]
Metal ion salts	Synthetic medium	$FeCl_2$	Anaerobic consortia	4000[a]	6.0	37	122.7 mL H_2 g^{-1} sucrose	[190]
	Synthetic medium	$FeCl_2$	Anaerobic sludge	500[a]	6.8	37	200[j]	[191]
	Synthetic medium	$FeCl_3$	*Enterobacter aerogenes* MTCC 111	213[a]	6.15	30	1.69[b]	[192]
	Synthetic medium	$FeSO_4$	Anaerobic sludge	350[a]	7.0	35	311.2[b]	[193]
	Palm oil mill effluent	$FeSO_4$	*Clostridium butyricum* EB6	309[a]	5.6	37	2.2[b]	[194]
	Whey permeate	$FeSO_4$	Anaerobic consortia	1500[a]	7.0	25	4.13[k]	[195]
	Synthetic medium	$FeSO_4$	Anaerobic consortia	3000[a]	5.5	35	1.9[b]	[196]
	Sweet potato	$FeSO_4$	Anaerobic sludge	63.17[a]	6.0	30	3501 mL H_2 L^{-1}	[146]
	Glucose	$FeSO_4$	Anaerobic sludge	200[a]	6.8	37	234.4[i]	[197]
	Synthetic medium	$FeSO_4$	Anaerobic sludge	100[a]	6.0	37	2.6[b]	[198]
	Synthetic medium	$FeSO_4$	Mixed consortia	100[a]	5.0	70	5.729 mL H_2 L^{-1} h^{-1}	[199]
	Synthetic medium	$NiCl_2$	Anaerobic sludge	0.1[a]	7.0	35	296.1[i]	[200]
	Synthetic wastewater	$NiCl_2$	Anaerobic sludge	16[a]	6.0	34	14.89 mol H_2 kg^{-1} COD_R	[201]
	Synthetic wastewater	$MgCl_2$	Mixed consortia	200[a]	5.4	55	1.75[b]	[202]
	Synthetic medium	$MgCl_2$	*Ethanoligenens harbinense*	600[a]	7.0	35	2.14[b]	[203]
	Sucrose	$CaCl_2$	Mixed consortia	100[a]	5.5	60	700[j]	[171]
	Sucrose	$CaCl_2$	Mixed consortia	5.4[a]	6.7	35	2.45[h]	[204]
	Sucrose	Na_2CO_3	Anaerobic consortia	1000–2000[a]	6.5	37	28.04–28.97 mL H_2 g^{-1} sucrose	[205]
	Glucose	NaCl	*Clostridium acetobutylicum* NCIMB 13357	5000[a]	7.0	30	–	[206]

Temp: Temperature, [a]mg L^{-1}, [b]mol H_2 mol^{-1} glucose, [c]mL H_2 g^{-1} VS, [d]mL H_2 g^{-1} COD, [e]mol H_2 g^{-1} COD, [f]L H_2 g^{-1} COD, [g]mol H_2 mol^{-1} xylose, [h]mol H_2 mol^{-1} sucrose, [i]mL H_2 g^{-1} glucose, [j]mL, [k]mol H_2 mol^{-1} malate.

[210]. Application of RSM involves these sequential steps: (i) experimental design using standard statistical DoE and implementation of the experimental design to collect data, (ii) development of empirical models using the experimental data and validate the developed model, (iii) use the developed and validated model to explain the parametric effects of the operating variables (individual and interaction) using response surface plots and contour plots (iv) predicts the optimal process conditions using the constraints set by the lower and upper limits of the independent variables of the validated model and with the validated model as the objective function, and (v) experimentally confirm the optimal conditions by comparing the experimental output with the model output [213].

Since the economic and industrial success of DF mainly lies in the optimization of operating conditions such as the nutritional composition, biomass concentration, hydraulic retention time, H_2 partial pressure, pH, and temperature [10,36,214,215], recent studies have been modelling and optimizing these parameters to determine the optimal operating variables that could be instrumental to the scalability of DF process [146,207,216]. These studies are usually conducted using renewable and inexpensive feedstocks such as industrial and municipal wastewaters, lignocellulosic biomass, and food waste as shown in Table 3.

Recently, Lopez-Hidalgo et al. [217] used the CCD to determine the optimal conditions for DF using a mixture of agro-industrial wastes i.e. wheat straw hydrolysate (WSH) and cheese whey (CW), alongside other parameters such as pH, temperature. The optimal conditions of 7.25, 26.6 °C, 5 g L^{-1}, and 25 g L^{-1}, were achieved for pH, temperature, WSH, and CW, respectively, and this produced a H_2 yield of 5724.5 mL H_2 L^{-1}. These optimal variables were then used in large-scale processes (1 L and 4 L) and produced a H_2 production rate of 66.6–89.5 mL H_2 L^{-1} h^{-1}. Similarly, CCD was applied in the optimization of H_2-producing variables (pH, potato concentrate, temperature, and fermentation time) [217]. Optimal H_2 yield of 68.54 mL H_2 g^{-1} TVS was obtained at optimized conditions of 7.86, 39.56 g L^{-1}, 37.87 °C and 82.58 h, for pH, substrate concentration, temperature, and fermentation time, respectively. Zainal et al. [218] studied the synergistic effects of reaction temperature, inoculum size to substrate ratio, and reaction time on H_2 yield using palm oil effluent via the statistical software (Design Expert® Software). A maximum H_2 yield of 28.47 mL H_2 g^{-1} COD was obtained at a reaction temperature of 50 °C, inoculum size to substrate ratio of 40:60, and reaction time of 8 h. Furthermore, these conditions achieved a COD removal efficiency of 21.95% [218]. CCD models are suitable in DF studies because the predicted (R^2) and adjusted (Adj. R^2) coefficient of determination values are usually high (>0.90) which implies that these models are adequate to describe the process and to navigate the optimization space [219].

BBD is another multivariate tool that has attracted a lot of attention in DF due to its excellent prediction ability (high Adj. R^2 and R^2 values) and its ability to use fewer experimental runs in comparison to the CCD model [220–222]. Rafieenia et al. [223] recently reported an innovative

Table 3
Summary of the predictive models that have been reported in H_2 production studies.

Substrate	Inoculum	DoE	Optimum conditions for H_2 production	H_2 yield	Reference
Food waste	Granular sludge	Box-Behnken Design	Initial pH of 5.5, pretreatment duration of 42.67 h, and waste frying oil conc. of 7.74 g L^{-1}.	71.34[a]	[223]
Growth medium	*Enterococcus faecium* INET2	Box-Behnken Design	Initial pH 7.1, temperature 34.8 °C, glucose concentration 11.3 g L^{-1}, and inoculation amount 10.4%.	1.29[b]	[224]
Sugarcane bagasse	Mixed anaerobic cultures	Central Composite Design	Substrate concentration of 22.77 g L^{-1} total sugar, substrate: buffer ratio of 4.31, and inoculum: substrate ratio of 0.31.	6980 mL H_2 L^{-1}	[252]
Sugarbeet molasses	Mixed consortia	Box-Behnken Design	Initial pH of 7.0, COD of 10 g L^{-1}, and volatile suspended solids of 4–20 g COD g^{-1} VSS.	2.3[c]	[253]
Potato starch	*Clostridium butyricum*	Box-Behnken Design	Substrate concentration of 15 g L^{-1}, buffer concentration of 5×10^{-2} mol m^{-3}, and inoculum ratio of 3.	6.4[b]	[254]
Growth medium	Psychrophilic strain G089	Box-Behnken Design	Temperature of 26.30 °C, initial pH of 6.2, and glucose conc. of 25.31 g L^{-1}.	1.81[b]	[255]
Potato waste	Mixed anaerobic cultures	Central Composite Design	Potato waste conc. of 39.56 g L^{-1}, initial pH of 7.1, temperature of 37.87 °C, and fermentation time of 82.58 h.	79.43[d]	[20]
Jatropha waste	Mixed anaerobic cultures	Central Composite Design	Substrate conc. of 211 g L^{-1}, temperature of 55.4 °C, and pH of 6.5.	296 mL H_2	[256]
Agricultural wastes	Mixed anaerobic cultures	Mixture Design	Optimal proportion of food waste, cattle manure, potato pulp and pig manure was 61.6%, 38.4%, 0%, and 0%, respectively.	21[e]	[239]
Growth medium	*Chlorella* sp.	Taguchi Design	Initial pH of 7.0, temperature of 35 °C, substrate conc. of 80 g VS L^{-1}.	22[e]	[257]
Fruit peels	Mixed anaerobic cultures	Plackett-Burman Design	C/N ratio of 30, temperature of 37 °C, and GAS as the best inoculum.	2221 mL H_2 L^{-1}	[258]
Glucose	Mixed consortia	Box-Behnken Design	Initial pH of 7.92, temperature of 32.9 °C, and glucose conc. of 17.0 g L^{-1}.	1.81[b]	[259]

C/N: carbon to nitrogen ratio, Conc.: concentration, COD: chemical oxygen demand, GAS: granular activated sludge, Conc.: Concentration, DoE: design of experiment, VS: volatile solids.
VSS: volatile suspended solids, TS: total solids, [a]mL H_2 g^{-1} VS, [b]mol H_2 mol^{-1} glucose, [c]mol H_2 mol^{-1} sucrose, [d]mL H_2 g^{-1} TVS, [e]mL H_2 g^{-1} VS.

approach of increasing the H_2 yield using mixed-consortia that was pretreated with waste frying oil. In this work, the waste frying oil was used to suppress the growth of H_2-scavenging microorganisms. The model was used to determine the optimum pH, pre-treatment time, and waste frying concentration. The model predicted complete inhibition of H_2-consumers at waste frying oil concentration of 7.74 g L^{-1}, fermentation pH of 5.5, and pre-treatment time of 42.67 h, respectively. And this led to a H_2 yield of 71.34 mL H_2 g^{-1} VS, which was 400% higher than the yield of the untreated inoculum [223]. Yin and Wang [224] produced a maximum H_2 yield of 1.29 mol H_2 mol^{-1} glucose and production rate of 86.7 H_2 L^{-1} h^{-1} at optimal variables of 7.1, 11.3 g L^{-1}, 10.4%, and 34.8 °C for initial pH, glucose concentration, inoculation amount, and temperature, respectively, using a newly isolated strain of *Enterococcus faecium*. Likewise, Sağır et al. [225] developed a sequential dark and photo-fermentative process in which the BBD method was used to optimize the process variables. A maximum H_2 yield of 7.8 mol H_2/mol glucose was achieved at a glucose concentration of 6×10^{-3} mol m^{-3}, inoculum fraction of 62.5%, and oxygen concentration of 4.5% using *Rhodobacter capsulatus* JP91 [225]. Therefore, these findings may provide new avenues for the development of integrated processes in DF. In addition to DF studies, the BBD model is widely used in other bioprocesses such as citric acid production [226], biomethane production [227], yoghurt production [228], bioethanol production [229], and sugar recovery from lignocellulosic biomass [230].

Factorial Design is also used to evaluate the effects of parameters on H_2 output [231]. This approach usually involves several combinations of different factor levels which allows it to predict the synergism between variables and enables it to be more effective in working with a large number of runs [232]. Factorial Design can be categorized into two groups i.e. Full Factorial Design and Fractional Factorial Design [232]. In Full Factorial design, all possible combinations of the process variables on H_2 yield are tested. The most commonly used Full Factorial design is the two-level design, which is represented by 2^n, where n refers to the number of process variables that are being evaluated by the model [233]. A polynomial regression model can also be generated to study the effects of the process conditions on H_2 response [233]. In contrast, the Fractional Factorial Design is employed when the number of experimental runs for a Full Factorial design is too many to carry out experimentally because of time and limited resources [234]. However, the Fractional Factorial Design may increase the experimental error, thereby compromising expected precision due to large experimental runs when compared to using BBD and CCD [207].

Other empirical tools like the two-level Plackett-Burman Design (PBD) have been used in the optimization of DF processes [235,236]. PBD is useful in screening the most influential parameters for bioprocess optimization [237]. After the screening process, a three-level experimental-design tool (e.g. BBD or CCD) is applied to evaluate the synergistic effects of parameters on the overall H_2 yield [238]. Meanwhile, the Mixture Design (MD) is a special experiment tool that is used to determine the optimum proportions of feedstocks for enhanced H_2 yields [239,240]. Sekoai and Gueguim Kana [240] used the MD to assess the optimum proportions of corn stalk (CS), bean husk (BH), and organic

fraction of solid municipal waste (OFSMW) on H_2 yield using mixed-consortia. Optimum H_2 yield of 56.47 mL H_2 g^{-1} TVS was obtained at a ratio of OFSMW: BH: CS = 30:0:0. Thereafter, the authors used the BBD to optimize the setpoints conditions of pH, temperature, substrate concentration, and hydraulic retention time (HRT), respectively [240]. The BBD predicted the setpoint parameters of 7.9, 30.29 °C, 40.45 g L^{-1}, and 86.28 h for pH, temperature, substrate concentration, and HRT, with a H_2 yield of 57.73 mL H_2 g^{-1} TVS [240]. Similarly, Shuang et al. [239] studied the optimal proportion of cattle manure (CM), food waste (FW), pig manure (PM), and potato pulp (PP) for augmentation of H_2 yield using MD. An enhanced H_2 yield of 21.0 mL H_2 g^{-1} VS was achieved at optimal ratio of FW: CM: PP: PM = 61.6:38.4:0:0. Therefore, these results highlight the significance of MD models in DF processes that use co-digested feedstocks.

Computational fluid dynamics (CFD) is a multi-dimensional tool that employs numerical methods to provide useful information about the hydrodynamics of processes [241–246]. CFD also provides in-depth information about the design of DF reactors and is used to evaluate the scalability of DF systems [247]. This method is used to improve mixing, heat transfer, mass transfer, and chemical reactions within a fermenter [248,249]. These aspects of a reactor design can be fine-tuned with CFD, rather than with one-dimensional equations i.e. although they are simpler, they are less accurate. Wang et al. [250] conducted a hydrodynamics assessment using CFD for an industrial-scale DF process. The results showed that several process barriers need to be overcome in industrial-scale reactors, including velocity heterogeneity and stagnation zones. The optimal operation was achieved using an impeller with a rotation speed of 0.67 Hz and diameter of 1600 mm [250]. Ding et al. [251] used CFD to obtain an optimum propeller speed of 0.83–1.17 Hz for economic DF process. These results demonstrate the possibility of using CFD for up-scaling the DF processes.

The non-linear nature of bioprocesses has limited the application of RSM-based models in DF processes [260]. Hence, experts are now shifting to models that can encapsulate this non-linearity to effectively optimize the DF processes [261]. Artificial neural network (ANN) is the most robust empirical approach for modelling and optimization of multifaceted and non-linear systems [262]. ANNs emulates the neurological functioning of the human's brain by arithmetically modelling the network structure of interconnected nerves [262]. The interest in ANNs stems from their exquisite properties such as self-learning, adaptability, high-speed processing, fault and noise tolerance, and remarkable information-processing ability [263]. ANNs are used in various disciplines such as engineering, forensic sciences, medicine, mining, climatology, economics, agriculture, and business [264,265].

Currently, these tools are being used to elucidate the non-linear behaviour of biogenic H_2 processes [262]. Whiteman and Gueguim Kana [266] conducted a comparative assessment of ANN and BBD for DF process using sugarcane molasses. The ANN and BBD generated the coefficient of determination (R^2) values of 0.91 and 0.75, respectively, at optimal conditions of 8.0, 35 °C, 150 g L^{-1}, for initial pH, temperature, substrate concentration, and different inoculum concentrations (15% and 10.11%) for ANN and RSM, respectively. Therefore, ANN exhibited a higher level of accuracy compared to BBD and this confirms the inability of RSM-based models to accurately capture the behaviour of complex non-linear microbial systems as highlighted above [266]. Similarly, Jha et al. [267] assessed the accuracy of BBD and ANN models in the optimization of H_2 yield and COD removal efficiency in an up-flow anaerobic sludge blanket reactor. ANN was the most reliable optimization tool compared to BBD and generated a high R^2 value of 0.99, whereas the BBD model produced an R^2 value of 0.90. Furthermore, an optimum H_2 yield of 0.90 mol H_2 mol^{-1} glucose and a COD removal efficiency of more than 80% was achieved using the ANN approach [267].

In another study, ANN was used to regulate a continuous DF process for 450 days [268]. The model optimized the non-linear relationships of setpoint parameters of pH, temperature, sucrose concentration, recycle ratio, alkalinity, metabolites concentration, oxidation-reduction potential, and hydraulic retention time. There was a high correlation between the predicted and experimental results [268]. Recently, ANN was also used in the optimization of DF using organic fraction of solid municipal waste as a substrate [269]. The optimal conditions for DF were 7.0, 35 °C, 8%, and 1:5, for initial pH, temperature, solid content, and mixing ratio, respectively, with R^2 value of 0.96 [269]. High prediction accuracies with R^2 values ranging from 0.90 to 0.99 are also reported in other DF studies [270–278]. Hence, these results highlight the suitability of ANNs in the optimization of H_2 yields and these tools will help researchers understand the multifaceted and non-linear nature of DF processes, which is crucial for future scale-up studies. However, the use of ANN in biofuels is still in its infancy and requires further investigations. Table 4 summarizes the abovementioned studies and other studies on the use of ANN in DF processes.

3.4. Consolidated bioprocessing for lignocellulosic H_2 production

The "food vs fuel" debate has reinvigorated an interest in the development of second generation biofuels owing to their socio-economic benefits [279,280]. Lignocellulosic wastes are highly studied in DF processes because they are ubiquitous (have a global yield of more than 1.3 billion tons per annum) and are rich in nutrients [281–284]. Also, the lignocellulosic feedstocks make the process of DF to be economically-viable [285,286].

The conversion of lignocellulosic biomass into H_2 involves three sequential steps: (i) the pre-treatment process which disrupts the crystalline structure of lignocellulosic biomass, (ii) the conversion of polysaccharides into monomeric sugars via the hydrolysis process, and (iii) the utilization of monomeric sugars by H_2-producers [287,288]. However, the use of lignocellulosic feedstocks poses several challenges. Firstly, the pre-treatment methods are energy-intensive and laborious [289]. Secondly, fermentative inhibitors such as aliphatic compounds, furan derivatives and phenolic compounds are released during the pre-treatment [290–292]. Furthermore, techno-economic studies have shown that more than 40% of the overall costs are derived from the pre-treatment steps [293]. Therefore, the success of DF using cellulosic biomass relies on the development of robust and cheap technologies [294,295].

Consolidated bioprocessing (CBP) is receiving increasing popularity for its cost-effectiveness and ability to generate high H_2 yields [296–298]. CBP is a single fermentation process that integrates the steps of enzymatic pre-treatment, hydrolysis of polysaccharides, and conversion of sugars into H_2 using microorganisms [299,300]. This integrated process is beneficial because it lowers the capital costs, reduces the fermentation periods, minimizes the risks of contamination, and produces high H_2 yields [301–305]. This process is undertaken using the native or recombinant method [305]. The native strategy uses cellulolytic enzymes that are found in predominant H_2-producing microorganisms such as *Clostridium* [306,307]. The recombinant strategy employs genetically-engineered strains to enhance the hydrolysis of biomass, resulting in high H_2 yields [308]. However, in an industrial setting, the recombinant strategy would not be ideal due to various constraints such as the need to sustain high-level expression of recombinant cellulolytic genes and there are high risks of contamination [308].

Several cellulolytic clostridial strains including *C. cellulolyticum, C. termitidis, C. cellulovorans,* and *C. thermocellum* [42,307,309,310], *Caldicellulosiruptor* sp. [311], *Thermoanaerobacter* sp. [312], *Thermoanaerobacterium* sp. [313], *Ruminococcus* sp., and mixed biofilm-forming communities from anaerobic mixed sludge [314], compost manure [315], and rumen gut [316] are used in CBP of lignocellulosic H_2 production. Amongst these, thermophiles are extensively studied in CBP of lignocellulosic H_2 production because they: (i) produce high H_2 yields (ii) use various cellulosic biomass, (iii) improve the rate of hydrolysis, (iv) enhance the metabolic rates due to improved mass transfer, (iv)

Table 4
Summary of studies that reported the use of ANN for optimization of H_2 production.

Substrate	Inoculum	Input parameters for ANN training and modelling	H_2 yield	R^2 value	Reference
Sugarcane molasses	Anaerobic sludge	Initial pH (4–8), molasses conc. (50–150 g L^{-1}), temperature (35–40 °C), and inoculum concentration (10–50%).	84.33 mL H_2	0.91	[266]
Growth medium	Anaerobic sludge	Temperature (30–45 °C), HRT (4–48 h), and cell immobilized conc. (50–100%).	0.90[a]	0.99	[267]
Growth medium	Mixed consortia	Initial pH (5.0–6.5), glucose: xylose ratio (0:5 to 5:0), inoculum size (0.04–0.1 g), and age of inoculum (0–24 h).	325–379[b]	0.99	[273]
OFMSW	Mixed consortia	Initial pH of 7.0, temperature of 35 °C, solid content of 8%, and mixing ratio of 1:5.	138.88 mL H_2 gm^{-1} VS	0.99	[269]
Growth medium	Mixed consortia	Temperature (30–48.4 °C), initial pH (6.0–9.0), and glucose conc. (10–34.4 g L^{-1}).	305.3[b]	0.99	[272]
Glucose	Mixed cultures	Initial pH (5.5–7.5), temperature (20–55 °C), substrate conc. (0.3–58.6 g L^{-1}), and biomass conc. (0.9–17.6 g L^{-1} COD).	382[c]	0.97	[270]
Cheese whey	*E. coli*	Initial pH (6.5–7.5), ORP (−0.1 to −0.5 V), and DCO_2 (0–90%).	745[c]	0.95	[271]
Agricultural wastes	Mixed cultures	Temperature (25–40 °C), initial pH (5–9), substrate types (xylose, glucose and sucrose), and substrate conc. (10–35 g L^{-1}).	305.3[b]	0.90	[274]
Growth medium	Mixed consortia	Influent bicarbonate alkalinity (1–3.5 g L^{-1}), HRT (3–30 h), and organic loading rate (10–90 g COD L^{-1} d^{-1})	1.40[a]	0.96	[275]
Distillery wastewater	Mixed cultures	Temperature of 34 °C, pH of 6.5, HRT of 24 h, and OLR (1–10.2 kg COD L^{-1} d^{-1})	1300 mL H_2 d^{-1}	0.98	[276]
Kitchen waste	Mixed consortia	Volumetric loading rate (0–4 kg COD L^{-1} d^{-1}), pH (5.0–6.0), temperature of 34 °C, alkalinity (0.5–1.0 g L^{-1}), and ORP.	11.5H_2 L^{-1} d^{-1}	–	[277]
Basal medium	Mixed consortia	Biochar conc. (0–8x10^{-5} g L^{-1}), Nickel conc. (0–2x10^{-4} g L^{-1}), pH (5.5–7.0), and dosage of microbes (24 × 10^{-3}-33 × 10^{-3} g L^{-1}).	234.1[b]	–	[142]
Growth medium	*Enterobacter* sp.	Initial pH (6.0–8.5), peptone conc. (2–7 g L^{-1}), and xylose conc. (8–18 g L^{-1}).	1.94[d]	0.99	[278]

-: Not available; Conc.: concentration, COD: chemical oxygen demand, DCO_2: dissolved carbon dioxide, HRT: hydraulic retention time, OLR: organic loading rate. ORP: oxygen reduction potential, VS: volatile solids, [a]mol H_2 mol^{-1} glucose, [b]mL H_2 g^{-1} substrate, [c]mL H_2, [d]mol H_2 mol^{-1} xylose.

reduce the formation of inhibitors, and (v) pave the way to reducing the operating costs [317,318].

Mixed-cultures are also desirable in DF because these microorganisms can: (i) utilize various lignocellulosic feedstocks, (ii) produce H_2 under mild fermentation conditions (ii) increase the conversion of substrates and metabolic reactions, (iv) favour the production of continuous H_2 fermentations, (v) participate in synergistic mechanisms, (vi) can be used without sterilization, and (vii) allow simultaneous saccharification and fermentation of biomass [319–321]. *Clostridium* species are the most studied microorganisms for CBP of lignocellulosic H_2 production because they have complex cellulose degrading-enzymes known as cellulosomes [322]. It has been shown that *C. clariflavum* consists of 160 carbohydrate-active enzymes whereas *C. thermocellum* encodes for over 70 carbohydrate-active enzymes [323,324]. Pérez-Rangel et al. [325] evaluated the effect of wheat-straw for CBP of H_2 production using four inoculum sources (anaerobic sludge, cow ruminal fluid, forest soil, and microbes found in wheat straw). The microflora found in wheat-straw produced the highest H_2 yield (7 mL H_2 g^{-1} VS) and this was attributed to the presence of cellulolytic fungi which improved the saccharification of wheat-straw while promoting synergism with H_2-producing bacteria [325].

Wang et al. [326] used human waste simulants for thermophilic CBP of biogenic H_2 production using mixed-cultures obtained from various sites (hot spring, wastewater treatment plant, and landfill compost). A high H_2 yield of around 4 × 10^{-3} mol H_2/g substrate was achieved using the consortium in the landfill compost [326]. Further microbial analysis showed that *Caldanaerobius*, *Caloribacterium*, and *Thermoanaerobacterium* sp. were the main H_2-producing species [326]. Carver et al. [327] also used four cellulosic feedstocks (microcrystalline cellulose Sigma Type 20, Type 50, Whatman filter paper, and cellulosic filter paper) in CBP of H_2 production at different temperatures (50 °C and 60 °C) from compost. Results showed that *Clostridium* and *Thermoanaerobacter* were the dominant cellulolytic species. CBP of lignocellulosic H_2 production could also be integrated with other bioprocesses as acetic acid and ethanol were produced [327]. Table 5a highlights the various studies that used mixed-cultures in CBP of lignocellulosic H_2 production.

Others studies used pure-cultures in an attempt to overcome the thermodynamic limitations in biological H_2 production. These include cultures from the genera *Clostridium*, *Enterobacter*, *Bacillus*, *Thermoanaerobacterium* and *Caldicellulosiruptor*, as shown in Table 5b [311, 328–331]. Optimal H_2 yields of 2.53 mol H_2/mol hexose and 3.8 mol H_2/mol hexose were reported using pure-cultures of *C. saccharolyticus* [311], and *T. thermosaccharolyticum* [331], respectively. Other thermophilic studies reported high H_2 yields that ranged from 1.5 to 3.3 mol H_2/mol hexose [307,332–336]. The elevated H_2 yields in pure-cultures are caused by the high substrate conversion efficiency, suppression of inhibitors, and enrichment of H_2-producers. Nevertheless, the scalability of DF processes using pure-cultures is still uncertain due to the complexity of these inoculum sources and high operational costs [305].

3.5. Biological H_2 methanation

The production of clean H_2 through the water electrolysis process is also receiving a lot of consideration [365–372]. The cost of electricity to produce H_2 is regarded as the main barrier that restricts the industrialization of H_2 technologies in the energy sector [373–377]. Biological H_2 methanation is a method that converts H_2 and CO_2 into CH_4 and it is derived from the Sabatier reaction. This approach is advantageous because there are already existing CH_4 gas infrastructures (e.g. natural gas pipelines) that are used for various applications such as chemical industry, mobility sector, power generation, and gas sector [378–382]. The biological process uses moderate temperatures (50–60 °C) and biowastes and is considered as the most suitable biogas upgrading method [383,384]. In this technology, biogas consisting of CH_4 (50–70%), is converted into high CH_4 content (≥95%) through the exogenous addition of H_2 and CO_2 into the methanogenic reactor [383–390]. Studies on this technology are quite recent and investigation of the effects of various process variables such as reactor design, pH, temperature, mixing, partial pressure, and inoculum sources on CH_4 concentration is reported (Table 6).

4. The potential of bioenergy in Sub-Saharan Africa

Several Sub-Saharan African countries are listed amongst the world's fastest-growing economies [411,412]. These nations need a thriving energy sector to cater for this rapid industrialization and population growth [411]. Biofuels will serve as a catalyst to strengthening the region's energy sector, infrastructural development programmes, rural development, and economic growth. In recent years, efforts have been made to fast-track the development of biofuel-related technologies in this region. But these initiatives are hindered by several issues such as lack of technical expertise, low funding opportunities, political interference, and scepticism surrounding biofuels [412]. The existing biofuel projects are under preliminary stages and few of these have reached commercialization (Table 7). Nevertheless, these studies will play a crucial role in the advancement of alternative fuels in this region due to the high availability of biomass resources and non-arable land.

A recent review by Adewuyi [28] showed that the pressing humanitarian issues such as food shortages, poor health care, and slow economic growth delay the advancement of biofuels in Sub-Saharan Africa because a majority of the budget is earmarked for improving the livelihoods of people. It was proposed that these nations should establish regulatory frameworks that allow various stakeholders (farmers, landowners, foreign investors, NGOs, and research institutions) to play an active role in biofuel development initiatives [28]. Furthermore, the environmental and social impacts of biofuels need to be thoroughly assessed to ensure that they do not affect other valuable resources such as water and biodiversity.

4.1. The South African scenario

South Africa does not have adequate waste management facilities [413]. Therefore, a large fraction of the country's waste is disposed on landfills and this causes various environmental issues [414]. More than 60 million tons of waste is produced each year [415], and this value will increase by more than 10 million tons over the next decade [416,417]. The conversion of waste into biofuels could help to address these issues. It is noteworthy to mention that biofuel-related technologies are in their early stages in South Africa and about 200 small-scale biofuel plants have been built and run, but this number is likely to increase in the next few years due to government policies aiming at strengthening the development of alternative fuels [418]. Fundamental research afforts on DF studies are also being expended in some South Africa institutions such as Durban University of Technology, University of the Witwatersrand, and the University of KwaZulu-Natal to contribute to the development of this technology [419–426].

5. The way forward: a proposed roadmap for surpassing the current process barriers

In spite of the enormous amount of research that has been conducted over the past years, major hurdles still need to be overcome to realize the potential of DF process as an alternative fuel. The proposed optimal technologies are mostly conducted under laboratory-scale conditions and have not been evaluated at large-scale. Secondly, scientists are currently investigating the individualistic effects of these technologies on DF pathways but are yet to examine the synergistic interactions of these technologies on H_2 yield from DF, and this stagnates the industrialization of DF technology. To accelerate the commercialization of DF process, the stakeholders (scientists, industries, and policymakers)

Table 5a
Consolidated bioprocessing of lignocellulosic H_2 production process using mixed anaerobic cultures.

Substrate	Inoculum	Temp (°C)	pH	Operation mode	H_2 yield	Reference
Leaves	Anaerobic cultures	37	7.0	Batch	37.8[a]	[337]
Rice husk	Anaerobic cultures	35	6.0	Batch	200 mL H_2 L^{-1}	[338]
Rice straw	Anaerobic cultures	35	5.01	Batch	14.54[a]	[339]
Algal bloom	Mixed cultures	35	6.0	Batch	24.96[b]	[340]
Sweet sorghum	Mixed cultures	35	4.7–5.5	Continuous	10.4 L H_2 kg^{-1} sweet sorghum	[341]
Potato waste	Mixed cultures	37.87	7.86	Batch	79.43[b]	[20]
Cassava starch	Mixed consortia	60	5.5	Continuous	249.3 mL H_2 g^{-1} starch	[342]
Napier grass	Rumen consortia	38	7.0	Batch	–	[343]
Rice straw	Anaerobic sludge	55	7.0	Batch	0.74 × 10^{-3} mol H_2 g^{-1} VS	[344]
Corn straw	Anaerobic sludge	35	4–8	Batch	68 mL H_2 g^{-1} corn straw	[345]
Rice straw	Mixed cultures	55	6.5	Batch	24.8 mL H_2 g^{-1} TS	[315]
Corn stover	Anaerobic consortia	35	5.5	Batch	2.84–3.0[c]	[346]
Raw paper sludge	Microflora from paper sludge	55	7.0	Batch	110.91[a]	[347]
Molasses	Mixed consortia	35	5.5	Continuous	1.47[c]	[348]
Cornstalk	Anaerobic cultures	55	6.0	Batch	48.7[g]	[349]
Cornstalk	Anaerobic consortia	60	7.0	Batch	155.4[b]	[350]
Fodder maize	Mixed microflora	35	5.2–5.3	Batch	62.4 mL H_2 g^{-1} maize	[351]
Perennial ryegrass	Mixed microflora	35	5.2–5.3	Batch	75.6 mL H_2 g^{-1} grass	[351]
Wheat straw	Anaerobic cultures	37	5.5	Batch	5.18–10.52[a]	[352]
Rice straw	Mixed consortia	55	7.0	Batch	21[a]	[353]
Grass	Anaerobic consortia	35	6.0	Batch	1.25 × 10^{-3} mol H_2 g^{-1} grass	[354]
Mushroom waste	Mixed cultures	55	8.0	Batch	0.73 × 10^{-3} mol H_2 g^{-1} TVS	[355]
Sugarcane bagasse	Mixed cultures	37	6.0	Batch	6980 mL H_2 L^{-1}	[252]
Sugarcane bagasse	Elephant dung	37	6.5	Batch	0.84 mol H_2 mol^{-1} total sugar	[356]
Corn starch	Mixed consortia	35	5.3	Continuous	0.51[c]	[357]

Table 5b
Consolidated bioprocessing of lignocellulosic H2 production process using pure cultures.

Substrate	Inoculum	Temp (°C)	pH	Operation mode	H_2 yield	Reference
Wheat straw	*Caldicellulosiruptor saccharolyticus* DSM8903	70	7.2	Batch	3.8[c]	[311]
Sweet sorghum	*Caldicellulosiruptor saccharolyticus* DSM8903	70	7.2	Batch	1.75[c]	[311]
Maize leaves	*Caldicellulosiruptor saccharolyticus* DSM8903	70	7.2	Batch	1.80[c]	[311]
Bagasse	*Caldicellulosiruptor saccharolyticus* DSM8903	70	7.2	Batch	2.30[c]	[311]
Silphium leaves	*Caldicellulosiruptor saccharolyticus* DSM8903	70	7.2	Batch	0.48[c]	[311]
Switchgrass	*Caldicellulosiruptor saccharolyticus* DSM 8903	65	7.2	Batch	0.0112[d]	[302]
Microcrystalline cellulose	*Caldicellulosiruptor saccharolyticus* DSM 8903	65	7.2	Batch	9.4[d]	[302]
Cornstalk	*Thermoanaerobacterium thermosaccharolyticum*	65	7.2	Batch	6.8[d]	[294]
Cornstalk	*Thermoanaerobacterium thermosaccharolyticum*	60	7.0	Batch	0.00347[e]	[294]
Wheat straw	*Thermoanaerobacterium thermosaccharolyticum*	60	7.0	Batch	0.00353[e]	[294]
Avicel	*Clostridium thermocellum* 27405	55	7.0	Batch	0.032[f]	[304]
Filter paper	*Clostridium thermocellum* 27405	55	7.0	Batch	0.02619[f]	[304]
Sugarcane bagasse	*Clostridium thermocellum* 27405	55	7.0	Batch	0.02352[f]	[304]
Sugarcane bagasse	*Clostridium thermocellum* ATCC 27405	55	6.99	Batch	0.09783[f]	[306]
Delignified wood fibers	*Clostridium thermocellum 27405*	60	6.8	Batch	1.6[c]	[307]
Corn-stover	*Clostridium cellulolyticum* DSM 5812	37	7.2	Batch	51.9 L H_2 kg^{-1} TS	[358]
Cornstalk	*Clostridium thermocellum* 7072	55	7.2	Continuous	61.4[g]	[359]
Mushroom	*Clostridium thermocellum* DSM 1313	55	5–6	Batch	73.90[f]	[360]
Sorghum bagasse	*Clostridium saccharolyticus* DSM 8903	72	6.8	Batch	2.6 mol mol^{-1} hexose	[359]
Starch	*Enterobacter aerogenes* NCIMB 10102	40	6.6	Batch	1.09 mol mol^{-1} substrate	[361]
Barley straw	*Caldicellulosiruptor saccharolyticus*	70	7.0	Batch	0.0312[f]	[362]
Bagasse hydrolysate	*Bacillus firmus* NMBL-03	38	6.8	Batch	1.29 mol H_2 mol^{-1} sugar	[363]
Distillers grain	*Clostridium thermocellum* ATCC 27405	60	7.2	Batch	0.00127[c]	[364]

-: no data, [a]mL H_2 g^{-1} VS, [b]mL H_2 g^{-1} TVS, [c]mol H_2 mol^{-1} glucose, [d]mol H_2 g^{-1} substrate, [e]mol H_2 g^{-1} substrate, [f]mol H_2 L^{-1}, [g]mL H_2 g^{-1} corn stalk.

Table 6
An overview of the biogas upgrading processes from various substrates.

Reactor type	Inoculum	Substrate	Gas mix	Temp (°C)	pH	CH_4 (%)	Reference
CSTR	Digested manure	Raw cattle manure	*in-situ*	55	7.2	65	[391]
CSTR	Digested manure	Manure and whey	*in-situ*	55	7.5	90.2	[392]
CSTR	Digested sewage sludge	Sewage sludge	*in-situ*	37	8.0	99	[393]
UASB	Mesophilic granules	Potato starch	*in-situ*	55	8.3	82	[394]
Batch reactor	Anaerobic digestate	Maize leaf	*in-situ*	52	7.0–8.0	89	[395]
CSTR	Anaerobic digestate	Straw	*in-situ*	38	7.89–8.43	76.8–100	[396]
Batch reactor	Anaerobic sludge	Food waste	*in-situ*	37 and 55	8.6	77.5–98.1	[397]
Batch reactor	Anaerobic sludge	Corn-stover biochar	*in-situ*	55	7.5–9.0	>90	[398]
CSTR	Anaerobic sludge	Wastewater	*ex-situ*	35	5.5	92	[399]
Trickle-bed reactor	Immobilized mixed cultures	Trace elements	*ex-situ*	37	7.2–7.4	98	[400]
Trickle-bed reactor	Immobilized mixed cultures	Trace elements	*ex-situ*	37	7.4–7.7	>96	[401]
UASB	Anaerobic digestate	Digested slurry	*ex-situ*	52	8.0	98	[402]
Batch reactor	Anaerobic digestate	Trace elements	*ex-situ*	65	7.7–8.2	92	[403]
Biofilm reactor	Anaerobic sludge	Trace elements	*ex-situ*	37	7.0–8.0	90	[404]
Up-flow reactor	Mixed cultures	Digestate	*ex-situ*	55	8.48	96.8	[405]
Trickle-bed reactor	Anaerobic sludge	Trace elements	*ex-situ*	55	7.0	98	[406]
Trickle-bed reactor	Anaerobic sludge	Trace elements	*ex-situ*	40	7.31–7.40	97.19	[407]
CSTR	Cattle manure	Potato starch	*in-situ* + *ex-situ*	53	8.3–8.5	95	[408]
Batch reactor	Mixed cultures	Basal medium	*in-situ*	37	6.0	96	[409]
CSTR	Anaerobic sludge	Basal medium	*ex-situ*	35 and 55	7.2	96	[410]

involved in alternative energies should have a precise roadmap for DF. The roadmap should include research and development (R&D) stage (as shown in this article), scale-up studies, which could pave the way for the industrialization of this process (Fig. 2). In this manner, the process barriers highlighted in Fig. 1 can then be overcome by implementing the steps (1, 2, and 3) that are presented and described in this roadmap. Some of the recommendations applicable here are also discussed in section 6.

6. Conclusions and recommendations for future studies

This article provides a critical review of recent technological methods that are used to enhance H_2 yields in DF process. Herein, novel biogenic H_2 optimization methods such as cell immobilization, nanotechnology, empirical optimization tools, and biogas upgrading from renewable H_2, are suggested to be the most promising methods that can be used to overcome the technical barriers facing DF process. However, most of the studies discussed in this article are still at the infancy stage and are far from commercialization. Since the industrialization of any process relies on its scalability, it is therefore crucial to develop a technology roadmap that will lead to the scalability of the DF process, as explained in section 5. To achieve this, several strategies should be adopted and some of these are suggested below:

- More DF studies should be conducted at pilot-scale using optimized continuous reactors coupled with various online-monitoring and regulating instruments such as pH sensors, temperature sensors, actuators, and oxidation-reduction potential probes. This will provide reliable process data that can be used for its large-scale production.
- Inoculum development remains a critical issue in the DF process. Research relating to metabolic engineering and bacterial encapsulation will help in the creation of oxygen-tolerant bacterial strains, inhibition of H_2-scavenging pathways, reduction of microbial contaminants, reusability of bacterial cells, extending the fermentation periods, maintaining anaerobic conditions, and increasing H_2 production yields in DF process.

Table 7
Biofuel projects in Sub-Saharan African countries [411,412].

Country	Feedstock	Biodiesel (L)	Bioethanol (L)	Biogas (L)
Benin	Cassava	–	2×10^7	–
Burkina Faso	Sugarcane	–	2×10^7	–
Côte d'Ivoire	Molasses	–	2×10^7	1000
Ghana	Jatropha	5×10^7	–	–
Guinea	Cashew	–	1×10^7	–
Mali	Molasses	–	2×10^7	–
Malawi	Molasses	–	1.46×10^8	1000
Kenya	Molasses	–	4.13×10^8	–
Ethiopia	Molasses	–	8×10^7	1000
Niger	Jatropha	1×10^7	–	–
Nigeria	Sugarcane	–	7×10^7	–
Sudan	Molasses	–	4.08×10^8	–
Swaziland	Molasses	–	4.80×10^8	–
Senegal	Molasses	–	1.5×10^7	–
Tanzania	Molasses	–	2.54×10^8	1000
Togo	Jatropha	1×10^7	–	–
Uganda	Molasses	–	1.19×10^8	–

-: data not available.

- There is still a dearth of knowledge about the microbial community structure and its impacts on acidogenic pathways during the DF process. Although high-throughput characterization tools are now used to unravel the microbial assemblages associated with DF processes, the variations in inoculums, feedstocks and operational conditions make our understanding of the microbiology impaired. Therefore, in-depth microbial screening studies should be conducted to understand the microbial communities involved during the course of DF processes.
- It has been shown that an integrated process involving dark- and photo-fermentation can produce a theoretical yield of up to 12 mol H_2 mol^{-1} glucose. However, preliminary studies have not achieved this yield. More studies should therefore be explored to evaluate the possibility of attaining this yield as this could lead to the scalability of microbial H_2 processes.
- The pretreatment of lignocellulosic biomass remains a huge barrier in DF process, therefore the establishment of inexpensive pretreatments methods will assist in the advancement of this bioprocess as the majority of the operational costs are used in the initial pretreatment steps in DF process.
- Techno-economic studies are still necessary to acquire deeper insights into the technical and economic scenario of DF processes, particularly when using different feedstocks and setpoint parameters. This information will be useful in energy planning, system design, and operation of DF facilities.
- It is recommended that similar units (e.g. L H_2 kg^{-1} or mL H_2 kg^{-1} substrate) should be used in DF processes, particularly when using biomass feedstocks so that the performances of DF processes can be easily compared and evaluated across studies.
- The use of H_2 purification methods will be necessary so that the H_2 from the DF process can be used in technologies such as fuel cells. However, this will only be feasible at large-scale after surpassing the current thermodynamic limitations.
- The DF process should be integrated with other renewable technologies such as biogas upgrading methods because there are already existing CH_4 gas infrastructures (e.g. natural gas pipelines) that are used for various applications such as chemical industry, mobility sector, power generation, and gas sector.
- Since there are already existing pilot-scale biorefinery demonstration plants that are used to produce different compounds, DF processes should also be integrated into biorefinery methods to enhance the energetic gains and make this process more competitive as other products can be produced from these integrated systems.
- A multidisciplinary collaboration of experts from different fields such as chemical engineering, electrochemical chemistry, biological sciences, and material sciences will be instrumental in overcoming the current thermodynamic limitations and this could ultimately lead to the scalability of DF processes.
- It is important to have a strong partnership between the academia and industry. This will pave the way for new technological

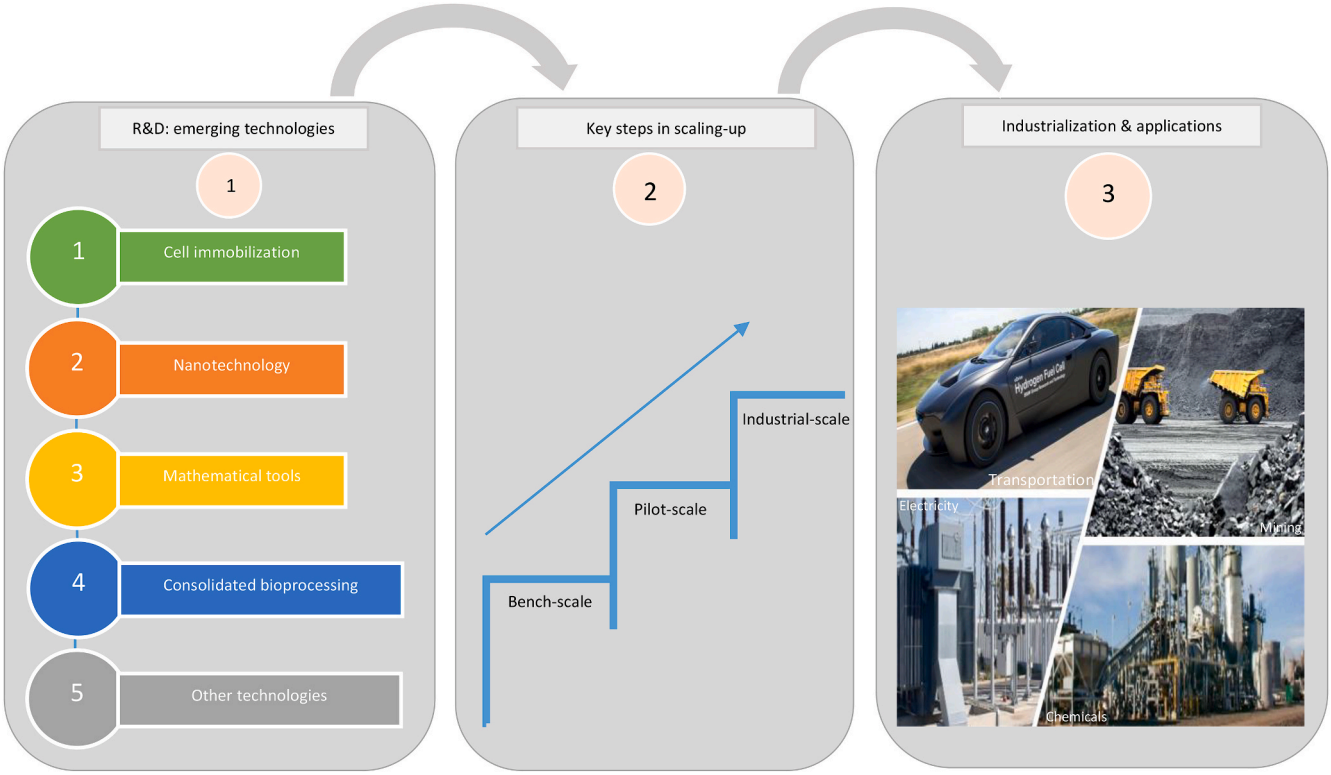

Fig. 2. Proposed roadmap for overcoming the current barriers hindering the commercialization of DF process. Adapted and modified from Hong et al. [427].

innovations which have a potential for commercialization. Furthermore, investments in scientific research, technological development, and scientific meetings will help to advance this field.

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