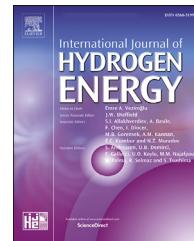




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Review Article

A meta-analysis of research trends on hydrogen production via dark fermentation

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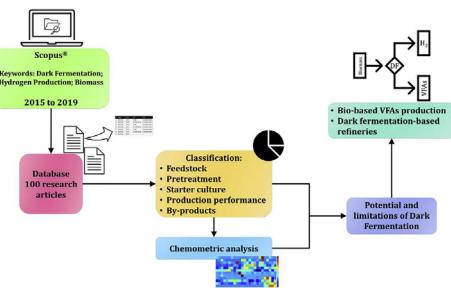
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HIGHLIGHTS

- Meta-analysis of research on H₂ and by-products production using dark fermentation.
- Clusters created based on feedstock, process conditions and productivity.
- Review of production strategies highlighting pros and cons.
- Discussion of challenges to integrating DF in large-scale bio-refining schemes.

GRAPHICAL ABSTRACT



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ABSTRACT

This work provides a meta-analysis of the state-of-the-art research on H₂ and value-added products production from biomass, via Dark Fermentation (DF) between 2015 and 2019. The meta-analysis data clusters are created considering inputs (i.e., feedstocks, and microorganisms used in DF), process conditions (i.e., feedstock pretreatments, and temperature, pH, working volume, substrate concentration in DF), yield and productivity of H₂ and the most common by-products (i.e., acetic, lactic, butyric, propionic acids and ethanol). Agricultural and green residues were the most common feedstock (36.5%), followed by Aquatic biomass (29.8%). Pretreated feedstocks and mixed cultures were employed in 72% and 79% of the studies, respectively. The meta-analysis relates H₂ high productivity to $6 \leq \text{pH} \leq 6.8$ and $35^\circ\text{C} \leq T \leq 37^\circ\text{C}$ and H₂ high yield to $5.5 \leq \text{pH} \leq 7.5$ under mesophilic conditions. The paper elaborates on the production strategies tested at the laboratory scale for each of the DF-products mentioned above, highlighting the pros and cons towards improving yield and productivity and discussing what are the challenges to integrating DF in large-scale bio-refining schemes for industrial production of H₂ and value-added products.

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Introduction

Energy is at the foundations of the technological and socio-economic development of contemporary society. This progress has been based on the use of fossil fuels, causing the increase of carbon dioxide (CO_2) in the atmosphere at an alarming rate with major impacts on the living conditions and the Earth climate. Therefore renewable energy is already a key factor for achieving the sustainable development of humankind [1,2].

Biomass is one of the major renewable sources of sustainable energy that can be efficiently stored in energy carriers, such as methane, hydrogen, ethanol, and biodiesel [3]. Hydrogen (H_2) is considered one of the most promising alternatives because of its net calorific value (120 kJ/g), which is the highest among renewable energy carriers. For example, the energy of 1 kg of H_2 is equivalent to the energy of 2.7 kg of petrol/gasoline or 6 kg of methanol [4,5]. Furthermore, H_2 is the cleanest fuel because its combustion releases only water and energy, with neither pollutants nor greenhouse gas emissions [6,7]. Biomass conversion into H_2 can be achieved thermochemically (e.g., gasification (500–1400 °C), pyrolysis

(300–1000 °C), combustion (650–1000 °C), liquefaction (200–300 °C)], and biologically (e.g., biophotolysis, photo-fermentation, dark fermentation) [8–12]. However, thermochemical processes are related to high equipment costs (CAPEX) with large energy requirements [13,14]. Besides, they can generate particulate matters and tar that affect the environment and human health [15]. Biological processes, in contrast, employ mild reaction conditions (30–80 °C at atmospheric pressure) with simultaneous H_2 production and waste recycling [16]. Among these biological alternatives, dark fermentation (DF) is a well-understood method with high H_2 production rates, and without light requirements [4,5,17].

H_2 –via DF– is produced by obligate anaerobic or facultative anaerobic microorganisms through their metabolic pathways under anaerobic conditions. In these conditions, oxygen is absent, and microorganisms must search for an alternate terminal electron acceptor, such as a proton. H_2 is produced when an electron is transferred to the proton. Biomass is converted into H_2 mainly via the acetate and butyrate pathways [18,19]. The maximum H_2 yield with the acetate pathway is 4 mol H_2 /mol glucose consumed. If the substrate is a pentose (e.g., xylose, arabinose), 3.33 mol H_2 /mol pentose are obtained. This is approximately equivalent to

588.5 mL H₂/g sugar¹ or 550 mL H₂/g COD.² If butyrate is the main metabolite, the maximum theoretical yield of H₂ is 2 mol H₂/mol glucose or 1.67 mol H₂/mol pentose. This is approximately 294.7 mL H₂/g sugar or 275.4 mL H₂/g COD. Details of pathways, stoichiometry and theoretical yields can be found in other excellent review papers published elsewhere [4,20].

DF using biomass (e.g., agricultural residues, algae biomass, alcohol industry effluents) as a substrate can be carried out by pure cultures, co-cultures, and mixed cultures at mesophilic temperatures (20–40 °C). Thermophilic (45–65 °C) and extremophilic (≥ 75 °C) cultures have been also studied [21,22]. During DF, a mixture of volatile fatty acids (VFAs) and solvents –such as acetic, lactic, butyric, propionic acids, and ethanol, among others– is produced, its composition depending on the operational conditions and the micro-organisms present in the culture. These compounds can be considered as value-added products since they are building blocks in the carboxylate platform which consider VFAs as intermediate feedstock chemicals [23,24]. In addition, the complex mixture of metabolites can be used in further biochemical or thermochemical processes (e.g., anaerobic digestion, photo fermentation, lipid production, purification), coupling DF as a reaction stage into biorefinery schemes based on biomass conversion [20,25–27]. The conversion of fermentative metabolites into complex expensive products (e.g., omega-3 fatty acids, polyhydroxyalkanoates, lipids), as well as bioenergy, is a breakthrough and promising option to create biorefinery concepts that support sustainable H₂ production via DF.

Research into H₂ production via DF using biomass as feedstock instead of simple fermentation media has increased dramatically over the past twenty years, as shown in Fig. 1. Despite the growing publication of research articles and reviews on DF, detailed quantitative comparisons and discussions of H₂ production approaches based on DF with different biomasses are missing in the published literature. Therefore, this study presents a Hierarchical Clustering Analysis (HCA) of the scientific literature published between 2016 and 2019 on H₂ production via DF considering inputs (i.e., feedstocks, and microorganisms used in DF), process conditions (i.e., feedstock pretreatments, and temperature, pH, working volume, substrate concentration in DF), and products production (i.e., H₂ and by-products production, yields and productivity). The meta-analysis identifies data clusters grouping similar H₂ and co-products production performances. DF by-products were also analysed as (a) value-added products, or (b) substrates for downstream processing. Finally, after identifying the current tendencies in the field, some issues that could take H₂ production by DF to industrial-scale are proposed to be explored.

Methodology

Database

The database used in this study was populated with records obtained from the Scopus® citation database and includes

¹ Sugar: glucose or xylose.

² COD equivalent of 1.07 g COD/g glucose or xylose [178].

documents published from 2015 to 2019. Documents were first selected by automatic queries based on the following keywords: Dark Fermentation; Hydrogen Production; Biomass. This led to the identification of 180 research articles. Records were removed from the database based on the following issues:

- Analytical grade carbohydrates as a substrate
- Analytical grade amino acids as a substrate
- Anaerobic digestion process alone
- Photo fermentation process alone
- Anaerobic solid-state fermentation process alone
- Microalgae cultivation process alone
- Non-JCR articles
- Non-experimental articles
- Reviews

The final database includes 100 research articles, whose records are included as part of the Supporting Information (Table S1). The discussion of H₂ and by-products production was enriched with other works also published in the scientific literature.

Feedstock classification

The feedstocks were classified into six categories according to their origin: Agricultural and green residues, Aquatic biomass, Industrial-derived products, Industrial effluents, and Municipal wastes. The description of each category –and sub-categories– is included in Table 1.

Pretreatment classification

The pretreatment methods used in the research articles included in the database were classified into four categories: physical pretreatment, chemical pretreatment, physicochemical pretreatment, and biological pretreatment. The description of each category is included in Table 2. The combination of two or more pretreatment methods in separate steps was considered as Sequential pretreatments. The combinations identified in those studies included in the database are defined as follows: physical → chemical, physical → physicochemical, physical → biological, and physical → chemical → biological. Examples of each are shown in Table 2.

Starter cultures

Starter cultures consist of microorganisms that are inoculated directly into bioreactors –of any working volume– containing feedstock which will be converted into H₂ and added-value products. In this work, starter cultures were considered as follows:

- Pure culture, culture containing a single microbial strain.
- Mixed culture, culture containing several microorganism species.
- Defined mixed culture, cultures containing microbiologically characterized strains, which are used as blends.
- Undefined mixed culture, cultures containing uncharacterized strains. They can include several genera, species, or even strains of microorganisms.

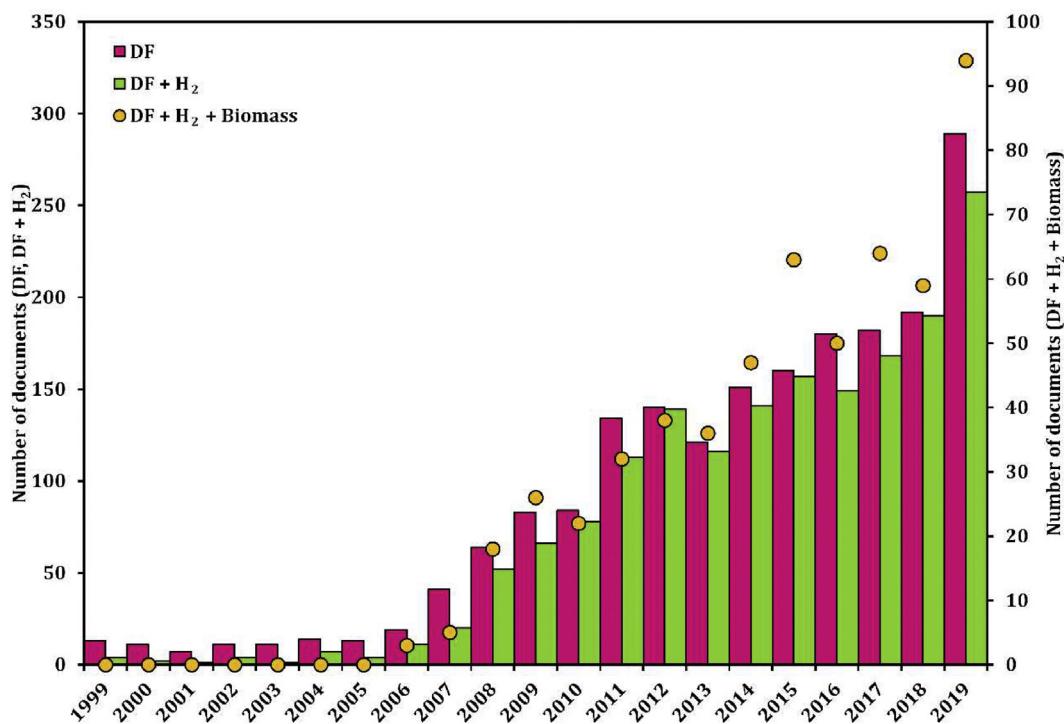


Fig. 1 – Publication of research studies related to hydrogen production from 1999 to 2019. DF, dark fermentation; H₂, hydrogen production.

Definition of response variables

Dark fermentation performance is characterized in this work with three main response variables:

- Hydrogen production (H_{2ac} , mL H₂/L) is defined as the amount of hydrogen produced per unit of culture volume. This variable was only considered for cases in which batch reactors were used.
- Hydrogen productivity (rH_2 , mL H₂/L·h) is defined as the amount of hydrogen produced per unit of culture volume per unit of time.
- Hydrogen yield (YH_2 , mL H₂/g substrate) is defined as the amount of hydrogen produced per unit substrate consumed at the end of the fermentation process.

If hydrogen production was reported in molar amounts, the value was converted using the ideal gases law. If production was reported as the hydrogen volume produced (in mL or L), values were divided by the reported working volume to obtain mL H₂/L for comparison purposes.

Data organization

Substrate concentration in DF experiments was reported in the reviewed articles using different units. Therefore, the production performance (H_{2ac} , rH_2 , YH_2) as a function of substrate concentration was divided into two main groups:

- G_1 , considering studies presenting substrate concentration as grams per litre of carbohydrate (monosaccharides and

disaccharides), total sugars, reducing sugars, chemical oxygen demand (COD), or total organic carbon (TOC). G_1 encloses 41 scientific articles.

- G_2 , encompassing studies reporting substrate concentration as grams per litre of total solids (TS), volatile solids (VS), or volatile suspended solids (VSS). G_2 encloses 37 scientific articles.

Chemometric analysis

Hierarchical Clustering Analysis (HCA) is usually employed to investigate similarities among objects in a given parameter space and, simultaneously, among parameters in the objects space [28–31]. The most popular similarity measures for continuous variables are the Euclidean distance, the Mahalanobis distance and the Manhattan distance. Regarding object linkage, five major methods are usually employed, namely the single linkage, the complete linkage, the average linkage, the centroid linkage as well as the Ward linkage.

The studied data were organized in two matrices: **X1** (24×12) and **X2** (21×11) where rows and columns represent objects (studied samples) and parameters (substrate concentration, temperature, pH, H_{2ac} , rH_2 , YH_2 , VFAs concentration), respectively. Matrix **X1** and matrix **X2** are included as part of the Supporting Information in **Tables S2 and S3**, respectively. The studied parameters for both matrixes are listed in **Table 3**. In matrix **X1**, the substrate concentration was reported as grams per litre of carbohydrate (monosaccharides and disaccharides), total sugars, reducing sugars, COD, or TOC.

Table 1 – Classification of feedstock used to produce hydrogen through dark fermentation.

Category	Description	Subcategory	Biomass source ^a
Agricultural and green residues	Plant-derived biomass with a combined structure of cellulose, hemicellulose, and lignin [251]. This category include: a) agriculture residues (materials left on the agricultural fields or orchards after the crop has been harvested and residual materials from the processing of the crop into a useable resource [252]), b) energy crops (crops cultivated specially to energy production [253]), c) green waste (conforming mainly by grass, leaves and fresh pruning originating from gardens and parks [254]; composting residues were also included as part of the green waste subcategory).	Agriculture residues Energy crops Green waste.	Straws (wheat, rice), stalks (corn, sunflowers), bagasse (sugar cane, agave, cashew apple), rice husk, wood, corn stover, pulps (carob, sugar beet), empty fruit bunch of oil palm, cassava residues, sugarcane top, <i>Jatropha curcas</i> seed cake Giant cane, sugar beet, <i>Paulownia</i> , energy poplar Fallen leaves, compost waste
Aquatic biomass	This category considers biomass produced by aquatic photosynthetic organisms [255,256].	Microalgae Seaweed Aquatic weed Cyanobacteria	<i>Scenedesmus obliquus</i> , <i>Chlorella</i> sp., <i>Chlorella vulgaris</i> , <i>Spirogyra</i> sp., <i>Keratococcus</i> , <i>Oscillatoria Saccharina japonica</i> , <i>Laminaria japonica</i> , <i>Sargassum</i> sp. <i>Pistia stratiotes</i> , <i>Eichhornia crassipes</i> , <i>Spartina anglica</i> <i>Microcystis wesenbergii</i> , <i>Microcystis aeruginosa</i> , <i>Arthrospira platensis</i> Cheese whey Molasses Wheat bran, malt powder, wheat starch
Industrial derived products	Feedstocks included in this category are products—not residues or wastes—defined by the European Commission in its (EU) 2017/1017 Regulations provided in the European Union Catalogue of Feed Materials [257].	Dairy products Agricultural products Cereal products	Vinasses (sugarcane, tequila, sugar beet)
Industrial effluents	Liquid streams generated by industrial processes containing concentrations of hazardous and toxic substances affecting receiving waters and the aquatic ecosystem [258–260]. The effluents considered here are not from domestic sources.	Sugar and ethanol industry effluents Industrial wastewater Other industrial effluents	Citrus fruit wastewater, nixtamalization wastewater, dairy wastewater Palm oil mill effluent (POME), crude glycerol
Municipal waste	The term municipal solid waste—which consists primarily of wastepaper (~20%), green waste (~13%), food waste (~15%), and plastic (~13%)—is commonly used to group solid wastes generated by human settlements from household activities [261–263]. However, it was not employed in this work because some of its components (i.e., green waste, food waste) were used as feedstocks in different research papers included in the database.	Wastepaper Sewage sludge	Wastepaper towel Solids residues from wastewater treatment
Food waste	This waste is generated during the food supply chain (food production, processing, distribution, storage, sale, preparation, cooking, and serving) [264]. Several definitions of food waste can be found in the literature [265,266]. In this work, food waste is defined according to the FUSIONS' Definitional Framework as any food removed from the food supply chain to be recovered or disposed of [267].	Domestic food waste Food industry waste	Vegetable peels, fruits peels, meat, fish, bread, rice, pasta Waste from fruit processing factories (mainly fruit pulp), expired solid baby foods

^a Based on information from the database.

Whereas in matrix X2, the substrate concentration was reported as grams per litre of TS, VS, or VSS. The analysis results were based on the Euclidean distance as a similarity measure and the Ward linkage algorithm which are common similarity

measures. Both of them are special cases of the Minkowski distance:

$$d_{ij} = \left[\sum_k (x_i - x_j)^g \right]^{\frac{1}{g}},$$

Table 2 – Classification of feedstock pretreatments using before hydrogen production through dark fermentation.

Pretreatment	Description	Examples ^a	Reaction conditions	References
Physical	Modify particle size, surface area, crystallinity, and degree of polymerization of biomass without using chemicals, enzymes, and microorganisms. Physical pretreatment may enclose milling, grinding, chipping, extrusion, ultrasonication, electric field, and irradiation [268,269].	Chipping Aqueous extraction	Size reduction (10–25 mm of diameter) Size reduction 1:2 S/L, 25 °C, 6h	[270] [51] [161]
Chemical	Exert conformational changes in the biomass structure –such as cleavage of bonds and generation of specific products– by the action of a chemical reagent. The techniques of chemical pretreatment comprise alkalis, acid, organosolv, ionic liquids, and oxidative processes [271,272]. Variants in which high pressure and/or temperature are used were also included in this category.	Acid hydrolysis Acid-thermal pretreatment	3% (v/v) H ₂ SO ₄ , 25 °C, 40 min 2% (v/v) H ₂ SO ₄ , 140 °C, 4 bar, 0 h 4 M HCl, 120 °C, autoclave, 30 min	[273] [274] [220]
Physicochemical	Combine physical changes and chemical reactions during processing. These pretreatments are performed at high temperature and/or pressure with an inorganic compound which leads to disruption of biomass structure. Common physicochemical pretreatments are steam explosion, ammonia fibre explosion, carbon dioxide explosion, liquid hot water, and hydrothermal liquefaction [275,276].	Hot-water hydrolysis Hydrothermal pretreatment Steam explosion	100 °C, 1 h 80 °C, 1.5 h 121 °C, autoclave, 15 min Pre-soak: 1% (w/w) H ₂ SO ₄ , 30 °C, 30 min 200 °C, 100 bars, 10 min	[277] [278] [279] [280]
Biological	Use of microorganisms (i.e., fungi, bacteria) or –either crude, pure or partially purified– enzymes (e.g., laccases, peroxidases, cellulases, hemicellulases) for the selective degradation of biomass components [281,282].	Enzymatic hydrolysis Microbial-enzymatic hydrolysis	80 U/g-biomass cellulose, 92 U/g-biomass α-amylase, 120 U/g-biomass glucoamylase, 50 °C, 12 h Bacillus sp., <i>B. sphaericus</i> , <i>B. subtilis</i> , <i>B. thuringiensis</i> , <i>Proteus mirabilis</i> strains (37 °C, 2 d)	[283] [284]
Sequential pretreatment				
Physical → Chemical	Involves the use of a physical pretreatment method followed by a chemical pretreatment method (e.g., milling followed by acid/base hydrolysis).	Milling → Alkaline hydrolysis Chopped → Acid hydrolysis	Size reduction (0.75 mm) 21% (v/v) MEA, 65 °C, 16 h	[285]
Physical → Physicochemical	Is a combination of a physical pretreatment method followed by another physicochemical (e.g., milling followed by steam explosion).	Comminuted → Microwave-acid pretreatment Milling → Steam explosion	Size reduction (2–3 mm) 2% (v/v) H ₂ SO ₄ , 121 °C, 15 lbs, 90 min Size reduction (<0.88 mm) 1% (v/v) H ₂ SO ₄ , 2450 MHz, 140 °C, 15 min Size reduction (<0.5 cm) 198 °C, 1.5 Mpa, 1.5 min	[286] [287] [288]

Physical → Biological	Grinding → Enzymatic hydrolysis	Size reduction (40-mesh) 1% (w/w) biomass, 1% (w/w) cellulase, pH 4.8, 50 °C, 150 rpm, 48 h [289]
	Grinding → Microbial-enzymatic hydrolysis	Size reduction (<40-mesh) Pretreated with <i>Phanerochaete chrysosporium</i> (29 °C, 21 d, 70% moisture) Enzymatic hydrolysis with <i>Trichoderma viride</i> [3.5% (w/w) biomass, pH 5.0, 50 °C, 130 rpm, 96 h] [162]
Physical → Chemical → Biological	Milling → Alkaline hydrolysis → Enzymatic hydrolysis	Size reduction (60-mesh) 0.5% Ca(OH) ₂ , 115 °C, 1.5h 2000 U/g-biomass cellulose, 2000 U/g-biomass xylanase, 50 °C, 10 h [219]
	Milling → Acid hydrolysis → Enzymatic hydrolysis	Size reduction (1–2 mm) 6% (w/v) H ₂ SO ₄ , 120 °C, 0.9 MPa, 60 min 1.17 mg cellulase/mL, 45 °C, pH 5.0 [160]

^a Based on examples from the database.

where g denotes the number of the variables (parameters). If g is equal to 2, d_{ij} is represented by the Euclidean distance. If g is equal to 1, d_{ij} represents the Manhattan distance. A colourmap was constructed as an interpretation of objects in the parameters space and parameters in the object space [32–34]. In the colourmap, all measured parameters are presented in the form of colour images with pixels representing the data matrix elements and sorted according to the order given. With the simultaneous interpretation of dendograms and the colourmap, relationships between operational conditions (e.g., temperature, pH, working volume, substrate concentration) and response variables (e.g., yields, productivity) were identified.

Conversion of biomass into hydrogen via dark fermentation

The biomass can be bio-converted into H₂ through DF by a wide variety of microorganisms [35]. Metabolic diversity enables microorganisms to use different biomasses as a substrate. The process to produce H₂ via DF using the biomass is sketched in Fig. 2A. A thermochemical pretreatment may be required before DF to make biomass sugars available to DF.

Table 3 – Studied parameters in the chemometric analysis.

A. Parameters considered in Matrix X1

No.	Parameter	Symbol	Unit
1	Substrate concentration ^a	S	g/L
2	Temperature	T	°C
3	pH	pH	—
4	Working volume	V _w	L
5	Hydrogen production rate	rH ₂	mL H ₂ /L·h
6	Hydrogen yield	YH ₂	mL H ₂ /g substrate ^a
7	Acetate	AcOH	g/L
8	Formate	FA	g/L
9	Lactate	LA	g/L
10	Butyrate	BTA	g/L
11	Ethanol	EtOH	g/L
12	Propionate	EtCO ₂	g/L

B. Parameters considered in Matrix X2

No.	Parameter	Symbol	Unit
1	Substrate concentration ^b	S	g/L
2	Temperature	T	°C
3	pH	pH	—
4	Working volume	V _w	L
5	Hydrogen production	H ₂ ac	mL H ₂ /L
6	Hydrogen production rate	rH ₂	mL H ₂ /L·h
7	Hydrogen yield	YH ₂	mL H ₂ /g substrate ^b
8	Acetate	AcOH	g/L
9	Butyrate	BTA	g/L
10	Ethanol	EtOH	g/L
11	Propionate	EtCO ₂	g/L

^a Substrate concentration reported as grams per litre of carbohydrate (monosaccharides and disaccharides), total sugars, reducing sugars, chemical oxygen demand, or total organic carbon;^b Substrate concentration reported as grams per litre of total solids, volatile solids total volatile solids or volatile suspended solids.

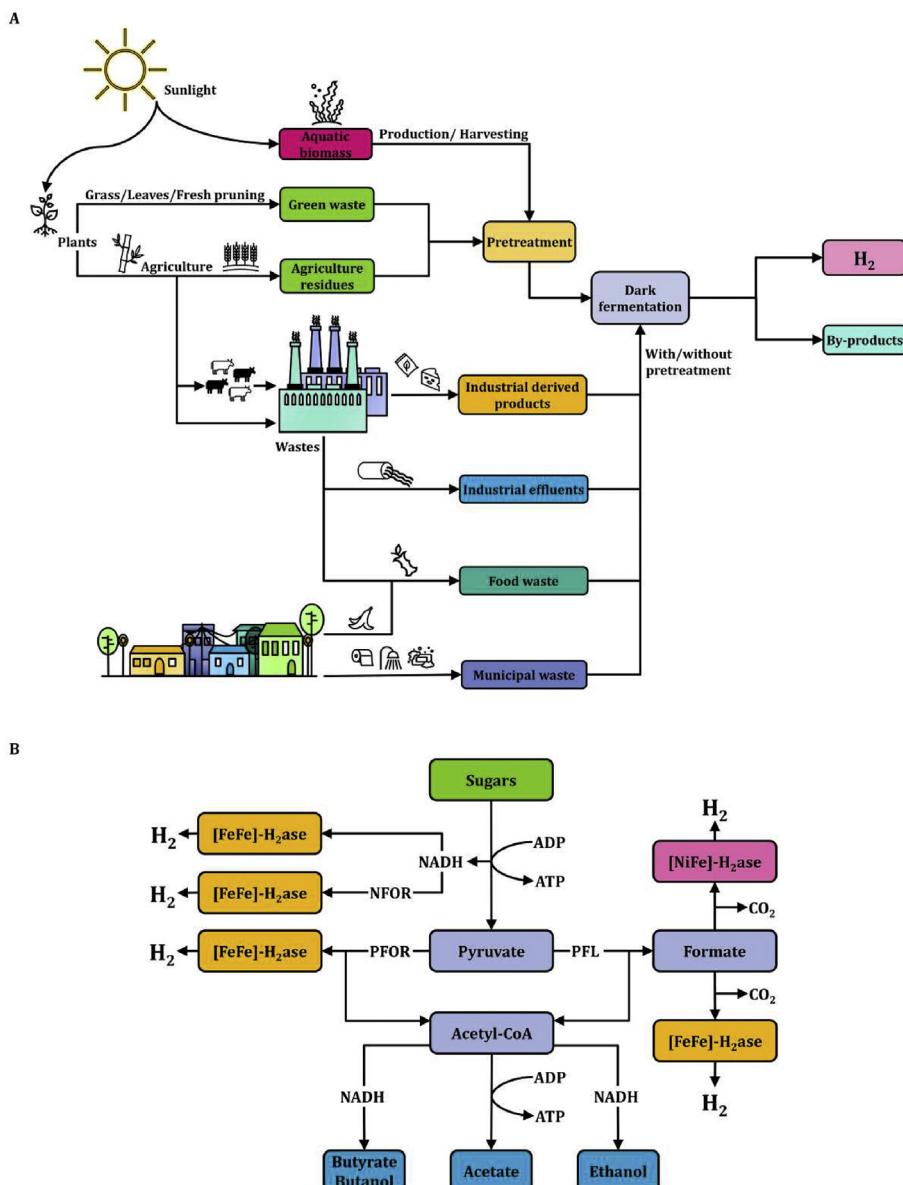


Fig. 2 – Production of hydrogen via dark fermentation from biomass. Biomass converted into H_2 , a general description (A). Typical metabolic pathways leading to H_2 production in dark fermentation [4,21] (B). NADH, nicotinamide adenine dinucleotide; NFOR, nicotinamide adenine dinucleotide hydrogen (reduced) ferredoxin oxidoreductase; PFOR, pyruvate ferredoxin oxidoreductase; PFL, pyruvate formate lyase.

Feedstocks employed in DF are composed of several components (e.g., carbohydrates, proteins, lipids), as described in Section [Feedstocks for hydrogen production](#). Carbohydrates can be hydrolysed into simple sugars, which are metabolized by certain bacteria to H_2 production. During DF, these sugars are converted into pyruvate via glycolysis (Fig. 2B), with the formation of nicotinamide adenine dinucleotide (NADH). In anaerobic conditions, pyruvate can be converted to acetyl coenzyme A (acetyl-CoA). This reaction can be catalysed by two different enzymes: a) pyruvate:ferredoxin oxidoreductase (PFOR), or b) pyruvate:formate lyase (PFL). If PFOR is used, the products are acetyl-CoA, CO_2 , and reduced ferredoxin. The latter is involved in the reduction of [FeFe]-hydrogenases, which subsequently reduce protons yielding H_2 . If PFL is

used, the products are acetyl-CoA and formate. The latter is converted to H_2 and CO_2 in the presence of [FeFe]-hydrogenases or [NiFe]-hydrogenases [4]. Further, acetyl-CoA can be converted into value-added products (e.g., ethanol, VFAs) with simultaneous oxidation of NADH and/or formation of adenosine triphosphate (ATP). Proteins are hydrolysed to amino acids (AA) by extracellular enzymes. Under anaerobic conditions, degradation of AA implies VFAs and ammonia production. This occurs using three pathways [36]: (i) Stickland reaction, (ii) oxidative deamination from a sole AA, (iii) reductive deamination from a sole AA (Table 4). Approximately 90% of AA degradation is controlled by the first reaction but it does not imply H_2 production. The second one, involving H_2 production, is thermodynamically unfavourable

Table 4 – Reactions involves in fermentation of proteins and lipids under anaerobic conditions.

Protein degradation		
Sticklan reaction		
Alanine + 2Glycine → 3Acetate + 3NH ₃ + CO ₂		
Oxidative deamination from a sole AA	ΔG° = + 4.2 kJ/mol	
Leucine + 3H ₂ O → Isovalerate + HCO ₃ NH ₄ ⁺ + 2H ₂		
Reductive deamination from a sole AA	ΔG° = - 77.8 kJ/mol	
Glycine + H ₂ → Acetate + NH ₃		
Lipid degradation		
n-LCFA → (n-2) -LCFA + 2Acetate + 2H ₂	ΔG° = + 48 kJ/mol	
Pyruvate + Acetate + 2H ₂ → CO ₂ + 3H ₂ O	ΔG° = - 95.4 kJ/mol	
LCFA: long chain fatty acids.		

unless H₂ partial pressure is maintained to an extremely low value. Although the third one is favourable, it is H₂ consuming. Even though proteins may enhance fermentation by providing nutrients for cell growth, degradation of AA involves H₂-consuming reactions [37]. The hydrolysis of lipids generates glycerol and long-chain fatty acids (LCFA). Glycerol can be converted into H₂ via DF. However, the degradation of LCFA is thermodynamically favourable (Table 4) under very low H₂ partial pressure (below 10⁻³ atm) [36]. Moreover, LCFA may inhibit anaerobic bacteria. They adhere to the cell wall restricting nutrient transportation [37]. Since higher YH₂ can be obtained with carbohydrates-rich feedstocks than with protein- and lipid-rich feedstock [38], the selection and evaluation of feedstocks for H₂ production is a crucial step for developing robust DF processes.

Table 5 – Description of feedstocks used for H₂ production via dark fermentation.

Feedstock		Characteristics	References
Agricultural and green residues		Available in large quantities (10–50 billion tonnes per year), low price, and renewable.	[99,290,291]
Aquatic biomass		Contain high amounts of carbohydrates Easy to cultivate and harvest. Achieve larger biomass production rates than terrestrial plants. Capacity to obtain high-added-value products.	[282,292]
Industrial derived products	Dairy products	Not part of the human food supply chain. Cheese whey. Worldwide estimated production of 10 ⁸ –1.9 × 10 ⁸ tonnes per year (10 L cheese whey/kg cheese). High lactose content, as well as nutrients for microbial growth.	[293,294]
	Agricultural products	Molasses. Available (~50 million tonnes worldwide production per year) and low cost, contain high amounts of sugar.	[295–297]
	Cereal products	Wheat bran (abundant and inexpensive) contain starch carbohydrates, arabinoxylan, cellulose, fructan, glucan, and proteins. Wheat starch is essentially carbohydrate, its minor components consisting of proteins, lipids, ash, and dietary fibre. Malt contains fermentable sugars, starch degradation enzymes, and nitrogen source for microbial growth.	[298,299]
Industrial effluents	Sugar and ethanol industry effluents	Wines are acidic suspensions of organic matter with high COD values, rich in phenolic compounds and melanoidins, containing minerals and small quantities of nonfermented sugar.	[300,301]
	Industrial wastewaters	Nixtamalization wastewaters (~12–14 million m ³ of wastewater per year, Mexico) contains high organic matter (COD and BOD), as well as carbohydrates, calcium, phenolic compounds, and proteins.	[302,303]
	Citrus wastewaters	Citrus wastewaters (1–17 m ³ per ton of citrus fruit processed) are rich in organic matter and nutrients, besides having a low pH and high corrosivity, could hold essential oils in trace.	[304–307]
	Dairy wastewater	Dairy wastewater (~6–10 L wastewater/L processed milk) have suspended solids, organic matter, high content of nitrogen and phosphorous, as well as oil and greases.	[312–314]
Municipal wastes	Other industrial effluents	Crude glycerol (0.1 kg glycerol/kg biodiesel produced) is an inexpensive carbon source for microorganisms growing and microbial products.	[315,316]
	Wastepaper	Palm oil mill effluent (3.05 ton/ton of crude palm oil produced) is rich in carbohydrates, proteins, nitrogenous compounds, minerals, and lipids.	[320–323]
	Sewage sludge	Lignocellulosic nature, abundant (represent approximately 20% of municipal solid waste) with low cost. Structurally it is composed of cellulose, hemicellulose, lignin, and filling materials (e.g. clay, calcium carbonate).	[321,324–326]
Food waste		Organic waste which may contain water, high BOD, nutrients (nitrogen, phosphorus, potassium, etc.), organic carbon, harmful pollutants (e.g., heavy metals, pharmaceuticals), and pathogens as well.	[327,328]
		Abundant (1.3 billion tonnes food per year) carbon source. May comprise a mixture of carbohydrates, lipids, and proteins.	[329–331]

The use of different biomasses as feedstock for DF is described below, followed by pretreatment methods and microorganisms employed to produce H₂.

Feedstocks for hydrogen production

As described in Section [Feedstock classification](#), the feedstocks were classified into six categories. [Table 5](#) includes a description of the feedstock categories considered in this work together with their associated references. The Agricultural and green residues, the most abundant renewable material on earth [[39,40](#)] was employed in 36.5% of the articles included in the database, as shown in [Fig. 3](#). Most of the feedstocks in this category were included in the subcategory of agricultural residues (79%). Energy crops and green waste are only employed by 13% and 8% of the studies considered in this category, respectively. These feedstocks are usually described in terms of biomass solids and moisture, as well as structural carbohydrates (*i.e.*, cellulose, hemicellulose) and lignin, as shown in [Table 6](#). Cellulose is usually embedded in a matrix composed primarily of lignin and hemicellulose. For

fermentative purposes, lignocellulose must be subjected to pretreatment to break the rigid lignin structure and hemicelluloses and to release cellulose for the enzymatic hydrolysis [[35,41](#)].

The second most important feedstock category is Aquatic biomass with 29.8% of the articles included in the database. Biomass from microalgae is studied in 52% of these articles, and the rest is almost equally distributed in biomass from aquatic weeds, seaweed, and cyanobacteria. They are usually described by their protein, lipid, and carbohydrates contents ([Table 7](#)). The lignin mass percentage ($\leq 20\text{ w/w}$) is usually lower than many agricultural and green residues, making its saccharification easier than of lignocellulosic biomass [[42,43](#)]. These feedstocks are also characteristic of fast-growing (compared to plants) and CO₂ fixation capacity (independent of arable land or freshwater), which makes them suitable feedstock for DF [[44–48](#)].

The rest of the feedstock categories presented percentages of 10.6%, 9.6%, 6.7% and 6.7% for Industrial derived products (by-products derived from manufacturing processes –not residues or wastes– whose composition depends on their

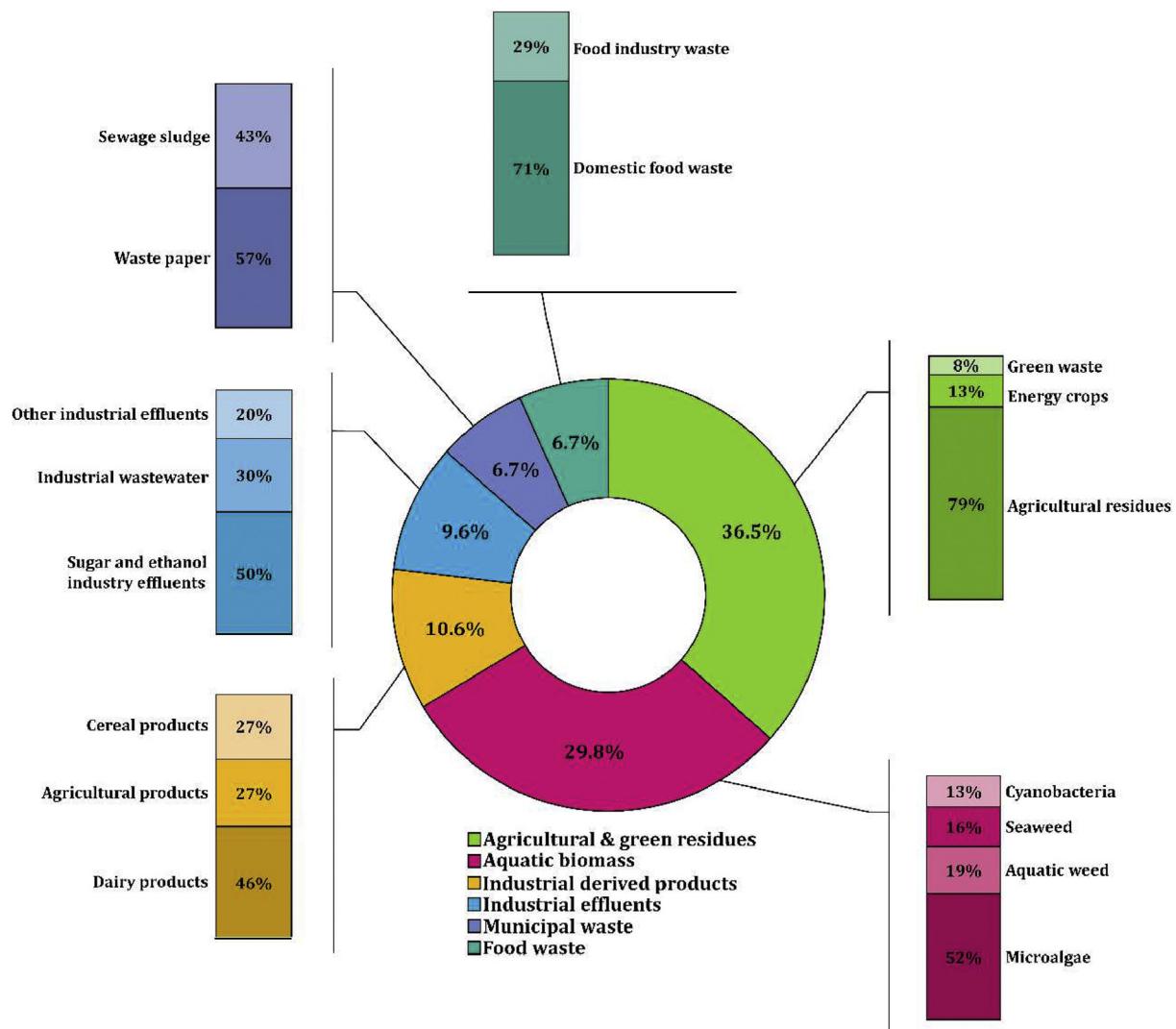


Fig. 3 – Feedstock commonly used to produce hydrogen with dark fermentation.

Table 6 – Composition (wt%) of agricultural and green residues.

Category	Subcategory	Biomass	Solids and moisture			Protein Lipid Extractives			Structural composition			Total Carb.	TOC	Elemental analysis	C/N	Reference
			TS	VS	Ash	Moist.	Cell.	Hemic.	Lignin	C	H	O	N	S		
Agricultural & green residues	Agricultural residues	Energetic willow wood					8.5	46.5	15.6	29.4					[285]	
		Pine tree wood pellet			1.3		0.1	39.5	22.1	37.1					[332]	
		Paulownia			4.3	13.0		34.6	19.3	15.9					[289]	
		Cornstalk			84.6										[219]	
		Rice straw						32.1	30.3	17.0					[286]	
		Rice husk			16.0		5.7	40.3	12.5	25.4					[163]	
		Rice straw	92.3	80.9											[333]	
		Wheat straw			93.5	89.4		44.5	19.2	5.8					[334]	
		Sugarcane top				7.5			39.0	20.0	21.5				[335]	
		Agave bagasse					17.5		56.4	10.9	15.2				[210]	
		Cashew apple bagasse	65.7	1.1	8.4			20.6	10.2	35.3					[336]	
		Sugarcane bagasse	91.8	1.9	8.2				42.3	21.0	18.4				[337]	
		Empty fruit bunch of oil palm			97.2	39.8	1.4	38.3	11.1	9.4					[211]	
		Cassava residues				5.5			47.6	16.3	19.5				[160]	
		Carob pulp				3.5	5.4	0.6			32.9	46.6			[270]	
Energy crops		Sunflower stalks	96.4 ^a	89.4 ^a				25.1 ^b	11.6 ^b	32.5 ^b					[161]	
		Jatropha curcas seed cake			867.8 ^c		13.7								[339]	
		Energy poplar			0.1	3.5		6.4–8.4	39.5	22.2	26.3				[116]	
Green waste		Giant cane							36.1 ^d	21.0 ^d	24.3 ^d				[340]	
		Fallen leaves	91.6	80.4			101.7 ^e					414.2 ^e			[243]	
					91.5				32.5	19.7	30.1				[341]	
	Green waste (compost waste)		657 ^c		24.0							39.0			[209]	
												200.0			[342]	

TS: Total solids; VS: Volatile solids; TOC: Total organic carbon; C/N: carbon-nitrogen ratio.

^awet weight %; ^bVS%; ^c g/kg substrate; ^d TS%; ^e mg/g-TS.

Table 7 – Composition (wt%) of aquatic biomass.

Category	Subcategory	Biomass	Solids and moisture						Protein	Lipid	FAME	Structural composition	Total Carb.	Elemental analysis					Reference		
			TS	VS	SS	DS	Ash	Moist.						C	H	O	N	S			
Aquatic biomass	Microalgae	<i>Scenedesmus obliquus</i>	92.4	88.4					20.2	22.6			55.4	44.3	7.8	44.3	3.2	0.4	13.7	[44]	
					75.5			5.4	20.4	17.1			0.3 ^a	1.4 ^a					20.2	[45]	
									35.7	25.2			30.7						[343,344]		
									31.4	17.9	4.4		42.6						[279]		
		<i>Chlorella</i> sp.	97.5	92.5			5.1	4.7	52.3	8.7			30.2						[345]		
		<i>Chlorella vulgaris</i>											29.2	47.2	6.5	30.2	8.4	0.6	5.6	[283]	
		<i>Spirogyra</i> sp.					5.4		23.2	14.2			45.6						[346]		
		<i>Consortia</i> (<i>Scenedesmus</i> , <i>Keratococcus</i> , <i>Oscillatoria</i>)							50.0	19.0			27.0						[347]		
		Undefined consortia	12.2 ^b	6.3 ^b									20.0						[214]		
		<i>Saccharina japonica</i>		82.8 ^d			80						43 ^c						[348]		
Seaweed		<i>Laminaria japonica</i>	98.3	82.8 ^d		17.2 ^d			15.6 ^f	0.8 ^f			998 ^e	40.1 ^f	5.5 ^f	45.6 ^f	2.5 ^f		[46]		
		<i>Sargassum</i> sp.	896 ^g	490 ^g					13 ^g				998 ^e	40.1 ^f	5.5 ^f	45.6 ^f	2.5 ^f	16.0	[287]		
Aquatic weed		<i>Pistia stratiotes</i>										32.9 ^f	11.7 ^f	3.3 ^f					[215]		
		<i>Eichhornia crassipes</i>	89.1	42.9	57.1	10.9	9.8					36.0	23.0	3.0					[48]		
		<i>Spartina anglica</i>	97.2	86.3		10.9	2.8					37.8	25.3						[273]		
		<i>Microcystis wesenbergii</i> , <i>Microcystis aeruginosa</i>		53.7		32.7	13.8		36.6	3.1		24.8	30.0	5.6	1.8 ^h	31.5	6.2	31.7	2.8	11.0	
		<i>Arthrospira platensis</i>		55.0		36.6			38.3	2.5		22.3	39.8	20.6						[115]	
Cyanobacteria												38.7 ^f	19.2 ^f	8.9 ^f						[349]	
															39.2 ^d	5.0 ^d	38.2 ^d	1.2 ^d	0.5 ^d	[139]	
															11.6	20.9	3.7	25.0	3.1	0.8	[212]
															15.1	24.1	4.9	25.3	2.6	0.8	[135]
															53.4					[138]	

TS: Total solids; VS: Volatile solids; SS: Suspended solids; DS: Dissolved solids; FAME: Fatty acid methyl esters; COD: Chemical oxygen demand; C/N: carbon-nitrogen ratio.

^ag/g-TS; ^b g/L; ^c mg/g; ^d TS%; ^e mg/g-TS; ^f VS%; ^g mg/g substrate; ^h g/g substrate.

origin, as shown in [Table 8](#), Industrial effluents (composed mainly of degradable organic matter which can be converted into H₂ by DF [49], see [Table 8](#)), Municipal (wastepaper and sewage sludge, see [Table 9](#)) and Food waste (see [Table 9](#) for composition details), respectively.

Feedstock pretreatment methods

Despite their complex structure, some feedstock can be converted directly into H₂ without pretreatment. According to the database of this work, 28% of the studies used unpretreated feedstocks to perform DF ([Fig. 4A](#)). The most employed feedstocks without pretreatment fall in Industrial-derived products and Industrial effluents categories. These feedstocks contain carbohydrates (e.g., lactose, sucrose, total carbohydrates, reducing sugars, glycerol) and organic matter that can be directly metabolized into H₂ by microorganisms such as *Clostridium* sp. and *Enterobacter aerogenes*, or by microbial consortia [50–54]. However, some feedstocks cannot be directly converted into H₂ due to their complex lignocellulosic matrix, which houses the sugars that can be metabolized by the microorganisms during DF. Thus, to make feedstock sugars soluble or biologically accessible for microbial conversion, feedstocks must be pretreated. Feedstocks in Agricultural and green residues and Aquatic biomass categories were usually pretreated, as shown in [Fig. 4A](#).

Pretreatments before DF can be employed alone or combined, as shown in [Fig. 4B](#). The different structural and compositional characteristics of each biomass results in a great diversity of pretreatment methods to achieve high sugars recovery, small amounts of degradation and fermentation-inhibition products with low energy requirements and environmental impacts capital (CAPEX) and operational (OPEX) costs [55,56].

According to the database, 40% of the studies employed a single pretreatment, whereas the rest used a combination of two or more pretreatment methods ([Fig. 4B](#)). Regarding single pretreatments, acid hydrolysis—in all its variants (i.e., room temperature, high temperature/pressure)—was the only chemical pretreatment employed alone. Other single pretreatments were heat pretreatment (i.e., high temperature, autoclavage conditions), hot-water hydrolysis and acid-steam explosion. Biomasses belonging to the Aquatic biomass category were mostly pretreated using single methods, as shown in [Fig. S1](#). Concerning sequential pretreatments (see Section [Pretreatment classification](#)), the combination of physical with chemical methods was the most employed (53%), as shown in [Fig. 4B](#). The combination of physical→chemical→biological pretreatments followed with 22% of the cases. In physical→chemical pretreatments, both alkaline and acid hydrolyses were the chemical methods that were combined with size reduction. For physical→chemical→biological pretreatment, the size reduction was combined with alkaline, acid hydrolysis or ionic liquids treatment followed by enzymatic hydrolysis (microbial or using enzymes). Regarding physical→biological pretreatments (13%), size reduction was followed by enzymatic hydrolysis (microbial or using enzymes). For

physical→physicochemical pretreatments (11%), acid-microwave assisted pretreatment, hydrothermal heating and steam explosion were the physicochemical techniques used after size reduction. Only feedstocks of Agricultural and green residues, Aquatic biomass, and Municipal wastes categories were treated using sequential pretreatments ([Fig. S1](#)).

Hydrogen-producing microorganisms

Dark fermentation uses anaerobic or facultative microorganisms that can degrade and convert biomass into H₂ and other by-products. The bacteria—22 different genus—reported for H₂ production in the research studies considered in the database are shown in [Fig. 5](#).

Clostridium was used in 38% of the studies, followed by *Enterobacter* (18%), *Bacillus* (8%), *Lactobacillus* (6%), *Escherichia* (4%), and *Streptococcus* (3%). The rest appear in less than 3% of the publications. *Clostridium* contains [FeFe]-hydrogenases and mainly uses the PFOR system for H₂ production [57]. However, *Clostridium* species such as *C. butyricum*, *C. acetobutylicum*, *C. beijerinckii*, *C. pasteurianum*, and *C. tyrobutyricum* can utilize the PFL system [58]. In facultative bacteria—such as *Enterobacter* and *Escherichia*—H₂ can be produced from formate via the PFL system by the action of [NiFe]-hydrogenases [59,60]. *Bacillus* isolates are capable to produce hydrogen using biomass—such as palm oil mill effluent (POME), food wastes, molasses and ethanol refinery wastewater—as substrate [61–64]. Also, some species of *Bacillus* such as *B. coagulans* can convert pyruvate to acetyl-CoA via the PFL system [65]. However, the effects on DF using mixed cultures *Bacillus* may be either positive (e.g., creating an anaerobic environment) or negative (e.g., increasing lactate concentration and decreasing H₂ production), which depends on operational conditions such as substrate concentration and temperature [66]. The presence of *Streptococcus* is mainly associated with auto aggregation of biomass by the accumulation of extracellular substances which maintain the structure of granules preventing their disintegration [67]. *Lactobacillus* is a lactic acid-producing bacterium and may compete with hydrogenic bacteria for the carbon source. Although both can co-exist, lactic acid-producing bacteria can reduce H₂ production at low substrate concentrations and short hydraulic retention times [68–71].

Dark fermentation can be carried out using either pure or mixed cultures. According to the database, 79% of the studies employed mixed cultures, whereas the rest employed pure cultures. Publications using genetically engineered microorganisms were not found in the literature with the keywords mentioned in Section [Database](#). While mixed cultures were reported using all feedstock categories, pure cultures were only reported in studies that employed biomass as the substrate of Agricultural and green residues, Aquatic biomass, and Industrial-derived products categories ([Table 10](#)).

Biomass conversion into H₂ using mixed cultures implies the participation of different microbial populations. Their interactions are of prime importance for efficient H₂ production. The microbial community structure may be affected by several factors, including pH, organic loading rate, carbon

Table 8 – Composition (wt%) of industrial derived products and industrial effluents.

Category	Subcategory	Biomass	Solids and moisture						Protein	Lipid	Extractives	Cellulose	Carbohydrates				
			TS	VS	SS	VSS	DS	Ash					Total Carb.	TRS	Lactose	Sucrose	Fructose
Industrial derived products	Dairy products	Cheese whey powder							13.3	1			76.5	75.5	70.0	75.5	154 ^a
			166 ^a	152 ^a											760 ^a	6.2 ^a	
	Agricultural products	Molasses							4–8				48–58				
	Cereal products	Wheat bran	92.5	95.4 ^b			140 ^a	121 ^a		0.7 ^a							
Industrial effluents	Sugar and ethanol industry effluents	Tequila vinasse ^a	34.5	30.9					6.2				68	14.5	8.2	19.6	11.0
		Sugarcane vinasse ^a	43.8	37.4				28.8	0.1			1.5		5.0	5.5		
	Industrial wastewater	Nixtamalization wastewater ^a	24.5	19.3					1.3				16.0	0.2			
		Citrus processing industry wastewater			0.6												3.9
	Other industrial effluents	Dairy wastewater	10.4		1.6			8.8		4.8	40.5						
		Crude glycerol															
		Palm oil mill effluent			18.8												

TS: Total solids; VS: Volatile solids; SS: Suspended solids; VSS: Volatile suspended solids; DS: Dissolved solids; TRS: Total reducing sugars; COD: Chemical oxygen demand; BOD: Biochemical oxygen demand; TOC: Total organic carbon; C/N: carbon-nitrogen ratio.

^ag/L; ^b TS%.

source, inoculum source, and inoculum pretreatment. Certain microbial species play a key role in the DF performance, thus its abundance may improve or decline H₂ production [72,73]. In undefined mixed cultures, the microbial diversity is usually dominated by *Clostridium* strains. Only few studies reported the dominance of *Enterobacter*, *Ruminococcus*, *Bacillus* or *Pectinatus* strains. Strains from *Ruminococcus* and *Pectinatus* genus have been also described as H₂ producers. *Ruminococcus* are rumen anaerobic bacteria with cellulolytic capacity that can produce acetic and formic acids, ethanol, H₂, and CO₂ from carbohydrates [74,75]. *Pectinatus* are butyrate-type fermentative bacteria, capable to adapt to brewery environments, producing mainly H₂, acetic and butyric acids from carbohydrates [76–78]. In 46% of undefined mixed cultures, *Clostridium* and *Enterobacter* strains appear together. The interaction between *Clostridium* and *Enterobacter* is beneficial to H₂ production since *Enterobacter* can remove oxygen and generate anaerobic conditions needed by strict anaerobes, such as *Clostridium* [66,79,80]. Although *Clostridium*/*Enterobacter* interactions are beneficial for H₂ production, other concomitant bacteria may accompany mixed cultures. Hydrogenic bacteria (e.g., *Lachnospira*, *Citrobacter*, *Enterococcus*, *Paraclostridium*), as well as bacteria with hydrolytic abilities or capacity to maintain an anaerobic environment (e.g., *Klebsiella*, *Burkholderia*, *Pseudomonas*), may be beneficial for H₂ performance. However, no-hydrogenic or hydrogen consumed or substrate competitor (e.g., *Terrisporobacter*, *Streptococcus*, *Lactobacillus*) bacteria can also be found in mixed cultures [66,81–84]. Their abundance is determined by operation parameters (e.g., pH, temperature, feedstock), source and pretreatment of inoculum, and process enhancement methods (e.g., additives, co-digestion, substrate pretreatment) [85].

Defined mixed cultures —i.e., synthetic/artificial microbial consortia or co-culture— involve the employment of complementary strains supporting each other activities, while some of them may possess hydrolytic capabilities, the others may have hydrogenic capacity. Thus, a potential synergy between the different involved strains is achieved, promoting operational stability and substrate consumption, as well as the increase of production yields [73,86,87]. Defined mixed cultures reported in the studies included in the database were *C. pasteurianum*/*B. subtilis*, *C. cellulolyticum*/*C. amalonaticus*, *E. coli*/*C. acetobutylicum*, *B. cereus*/*B. pumilus*/*Bacillus sp.*/*B. thuringiensis*/*E. aerogenes*/*P. mirabilis*, and *E. coli*/*E. cloacae*, using sugarcane bagasse hydrolysate, pretreated corn stover, cyanobacteria hydrolysate, food waste hydrolysate, and crude glycerol as substrate, respectively.

Among all microbial genera reported, only *Clostridium*, *Enterobacter*, *Bacillus*, *Pseudomonas*, *Proteus*, *Paraclostridium* and *Caldicellulosiruptor* were employed as pure cultures. *C. lento-cellum*, *C. roseum*, *C. butyricum*, *C. pasteurianum*, *Clostridium sp.*, *E. aerogenes*, *B. cereus* and *Proteus mirabilis* were used to convert biomasses of Agriculture and green residues category into H₂. *C. butyricum*, *E. aerogenes*, *Pseudomonas aeruginosa* and *Caldicellulosiruptor saccharolyticus* were employed in fermentations with feedstocks of the Aquatic biomass category. And *C. acetobutylicum* was used to obtain H₂ from molasses belonging to the Industrial-derived products category.

Production performance

Several operational parameters can influence yields and productivities during DF. This section is dedicated to describing the

Carbohydrates		Organic matter			N	C/N	Glycerol	Acetate	Propionate	Lactate	Butyrate	i-Butyrate	Ethanol	Methanol	Na	Minerals	Reference
Glucose	Starch	COD	BOD	TOC													
																	[350]
																	[150]
																	[334]
																	[58]
																	[136]
																	[236]
																	[351]
																	[165]
																	[352]
																	[109]
																	[164]
																	[110]
																	[111]
																	[109]
5.8 ^b	176 ^a	28–34	0.2–2.8														
63.7	1331 ^a			16 ^a													
				2.6 ^b													
					16.9												
						17.7 ^a											
							28.7 ^a										
								51.1 ^a									
									2.5 ^a								
										2.2 ^a							
59.7	30.6	15.8	0.2														
63.1	29.2		0.2														
49.0	23.2																
32.3	15.4																
25.1	14.0	8.7	0.4														
12.5	19.5																[112]
11	7.2																[353]
49.8	22.5		4.3														[113]
							47.5										[354]

H_2 production performance, considering operational conditions (temperature, pH, working volume), feedstock, as well as productivities and yields. According to the database, the average value of temperature (T) used was 36.9 ± 7.2 °C. Fig. 6A shows the distribution of incubation T according to feedstock, being the lowest and highest 24 °C and 70 °C, respectively. 83% of the studies used T between 34 °C and 40 °C, 10% of the studies used 26.6 °C or 30 °C, and only 7% used 55 °C or 70 °C. DF is usually carried out in mesophilic conditions despite the higher YH_2 obtained at thermophilic conditions [88,89]. This is mainly due to the structure and composition of the microbial community. For example, a microbial community dominated by *Thermoanaerobacterium* (in thermophilic conditions) obtained 1–2 fold more H_2 than a mesophilic community dominated by *Clostridium* [90]. However, DF must operate at near-ambient temperatures to obtain a positive net energy gain³ [91].

pH may affect substrate hydrolysis, hydrogenase activity and the metabolic pathways, as well as microbial community structure during DF [92]. Fig. 6B shows the pH as a function of feedstock, the average value was 6.4 ± 0.9 . According to the database, pH values employed were a) 4–4.25 in 2% of the studies, b) 5–6.5 in 52% of the scientific articles, c) > 6.5–8 in 43% of the studies, and d) >8–10 in 3% of the studies. Although hydrogenic pathways are usually established at pH values approximately 4.5–6.5, initial pH may influence H_2 production [93]. For example, in studies using different substrates (duckweed [94], kitchen waste [95], liquid scotta permeate [96], cattle slaughterhouse wastewater [97]), the initial pH, which improves H_2 production, was reported in the range of 7–8.5.

³ Defined as the total energy produced equivalent to the H_2 volume generated by DF minus any heat energy required to raise the reactor contents from ambient temperature to the fermentation temperature.

T and pH play an important role in DF because H_2 production can be inhibited if these variables do not have appropriate values [98]. Furthermore, optimal conditions of T and pH may depend on the type of substrate and source of inoculum used [99].

Conversion of biomass into H_2 can contribute towards future energy needs. However, studies at pilot and large scales must be carried out to prove the profitability of H_2 production via DF [100]. According to the database, the average working volume (V_w) employed was 0.6 ± 1 L. All feedstocks were mainly fermented in V_w between 0.016 and 1.2 L, as shown in Fig. 6C. Few studies were found with V_w between 1.5 and 4.5. Only one work reported a V_w of 200 L (not included in the plot). In addition, DF was performed mainly in batch operation mode (85% of the studies). Continuous and semi-continuous operation modes were employed in 14% and 1% of the studies, respectively. Batch operation is mainly used to evaluate kinetic and stoichiometric parameters, different substrates, as well as to perform inhibition assays [67]. The most used continuous reactors are continuous stirred-tank reactor (CSTR), granular sludge bed reactor (GSBR), fixed bed reactor (FBR), and sequencing batch reactor (SBR). According to the database, in studies that employed continuous mode operation, the CSTR was the most used (42.8%). On the one hand, CSTR is easy to design and operate. On the other hand, it has low biomass retention, with a prevalence of methanogens and unstable microbial diversity [101]. The second most utilized configuration was FBR (28.6%). An advantage of these reactors is biomass retention. However, liquid-gas mass transfer is limited and excessive microbial growth can occur [67,101]. SBR and GSBR were employed in 21.4% and 4.2% of the works, respectively. The advantages of SBR are diverse control strategies, decoupling solid and hydraulic retention times, usage of a large variety of instrumentation, flexible operation, and low cost. Their disadvantages are related to microbial

Table 9 – Composition (wt%) of municipal waste, food waste and fermentation outputs.

Category	Subcategory Biomass	Solids and moisture				Protein	Lipid	Lignin	Total Starch	COD	BOD	TC	TN	TP	Elemental analysis	C/N Reference	
		TS	VS	SS	VSS												
Municipal waste	Wastepaper	18.5 ^c	12.0 ^c													569.0 ^a 0.5 ^a <10-3 ^a	[355]
	Sewage sludge	6.4	4.0													569.0 ^b 470.0 ^b 1.0 ^b	[203]
Food waste	Domestic food waste	25.3	23.8			92.4	357.0 ^d	94.0 ^d								29.8 5.2 5.5 5.4	[341]
		7.5–12.6	6.5–11.5			13.7 ^c 12.2 ^c	1.2 ^c	491.0 ^e	5.2 ^e	142.0 ^e							[356]
		11.6–16.9	8.4–15.0				84.5–92.1 1.8–3.7 ^f			6–12.5 ^g							[357]
		19.6 ^g	17.8 ^g				78.3 ^g	10.5 ^g	6.2 ^g	42.7 ^g	40.6 ^g						[358]
	Food industry waste	34.2	98.0			13.4 ^c 10.8 ^c	0.6	65.8		4.7	12.4 ^c	26.4	55.2	55.2	0.2	0.1	[356]
																	[359]
																	[173]
																	[360]
																	[277]

TS: Total solids; VS: Volatile solids; SS: Suspended solids; DS: Dissolved solids; COD: Chemical oxygen demand; BOD: Biochemical oxygen demand; TC: Total carbon; TN: Total nitrogen; TP: Total phosphorus; C/N: carbon-nitrogen ratio.

^a g/kg^b mg/g-VSS; ^c g/L^d mg/g-TS; ^e mg/g-VSS; ^f mg/g substrate; ^g g/100 g substrate; ^h g/g substrate.

community structure (methanogenic archaea, homoaceto-genic bacteria, and propionic and lactic acid bacteria) [101,102]. GSBR is characterized by biomass retentions through the formation of self-aggregated granules. Nevertheless, the formation of these granules depends on the presence of exopolysaccharide forming microbes [101,103].

As explained in Section [Data organization](#), the data was organized into two groups, G₁ and G₂, to facilitate its analysis. In G₁, most studies employed substrate concentrations (S) ranging 0.6–36.9 g/L. Few studies were found with S surpassing 46 g/L. The average was 16.1 ± 14.4 g/L, as shown in [Fig. 7A](#). Regarding H₂ac, studies in G₁ reported the lowest and the highest value of 50 and 7092.9 mL H₂/L, respectively. The average was 2350.9 ± 2062.9 mL H₂/L, as shown in [Fig. 7B](#). Concerning rH₂, [Fig. 7C](#) shows that studies in the G₁ group reported values from 2.7 to 483.3 mL H₂/L·h, with an average of 108 ± 108.7 mL H₂/L·h. Regarding YH₂ ([Fig. 7D](#)), G₁ includes studies with values between 10 and 433.7 mL H₂/g substrate, with an average of 230.1 ± 125.6 mL H₂/g substrate. The YH₂ exhibits a decreasing trend as S increases for Agricultural and green residues, Aquatic biomass, and Municipal waste categories as shown in [Fig. S2A](#). This behaviour may be a response to the fact that an increase in S may reduce the substrate degradation efficiency, leading to a reduction in H₂ production [104,105].

Moreover, studies using different biomasses –such as food waste [106], waste paper [107]– concluded that increasing S enhances H₂ production up to a certain limit. The effect of S may also depend on the type of starter culture used. Some microorganisms possess high hydrogenase activity, thus using a larger substrate amount than those with low hydrogenase activity [108]. However, using cheese whey powder as feedstock –which is classified in the Industrial-derived products category– was obtained a high YH₂ (296.8 mL H₂/g substrate) at high S (46.4 g/L) [58]. Moreover, studies that employed feedstocks from the Industrial effluents category reported YH₂ values between 416.7 and 423.8 mL H₂/g substrate at relative low S values (5–24 g/L) [109–113]. YH₂ seems to increase as rH₂ increases in studies using biomasses of Agricultural and green residues, Industrial-derived products, and Industrial effluents categories ([Fig. S3B](#)). However, when feedstocks of the Aquatic biomass category were employed as the substrate, YH₂ seems to decrease as rH₂ increases. For instance, the lowest rH₂ (14.1 mL H₂/L·h) was accompanied by a relative high YH₂ (339 mL H₂/g) [114]. Also, the lowest YH₂ (41.4 mL H₂/g) was obtained together with a relative high rH₂ (222.8 mL H₂/L·h) [115]. However, a study in which microalgae was employed as feedstock [44] reported a high YH₂ (391.5 mL H₂/g) with a high rH₂ (1916 mL H₂/L·h, not included in the plot). Therefore, there is necessary more data to establish a clear relationship between YH₂ and rH₂ when feedstocks from the Aquatic biomass category are used.

The studies included in G₂ employed S between 1.9 and 47.3 g/L. The average value was 18.4 ± 12.9 g/L, as shown in [Fig. 7A](#). For H₂ac, the lowest and the highest value were 107.5 and 4862 mL H₂/L, respectively. The average H₂ac was 986.6 ± 1198.6 mL H₂/L, as shown in [Fig. 7B](#). Concerning rH₂, [Fig. 7C](#) shows that the data ranges were from 2.6 to 162.8 mL H₂/L·h. The average was 46.3 ± 51.4 mL H₂/L·h. Regarding YH₂

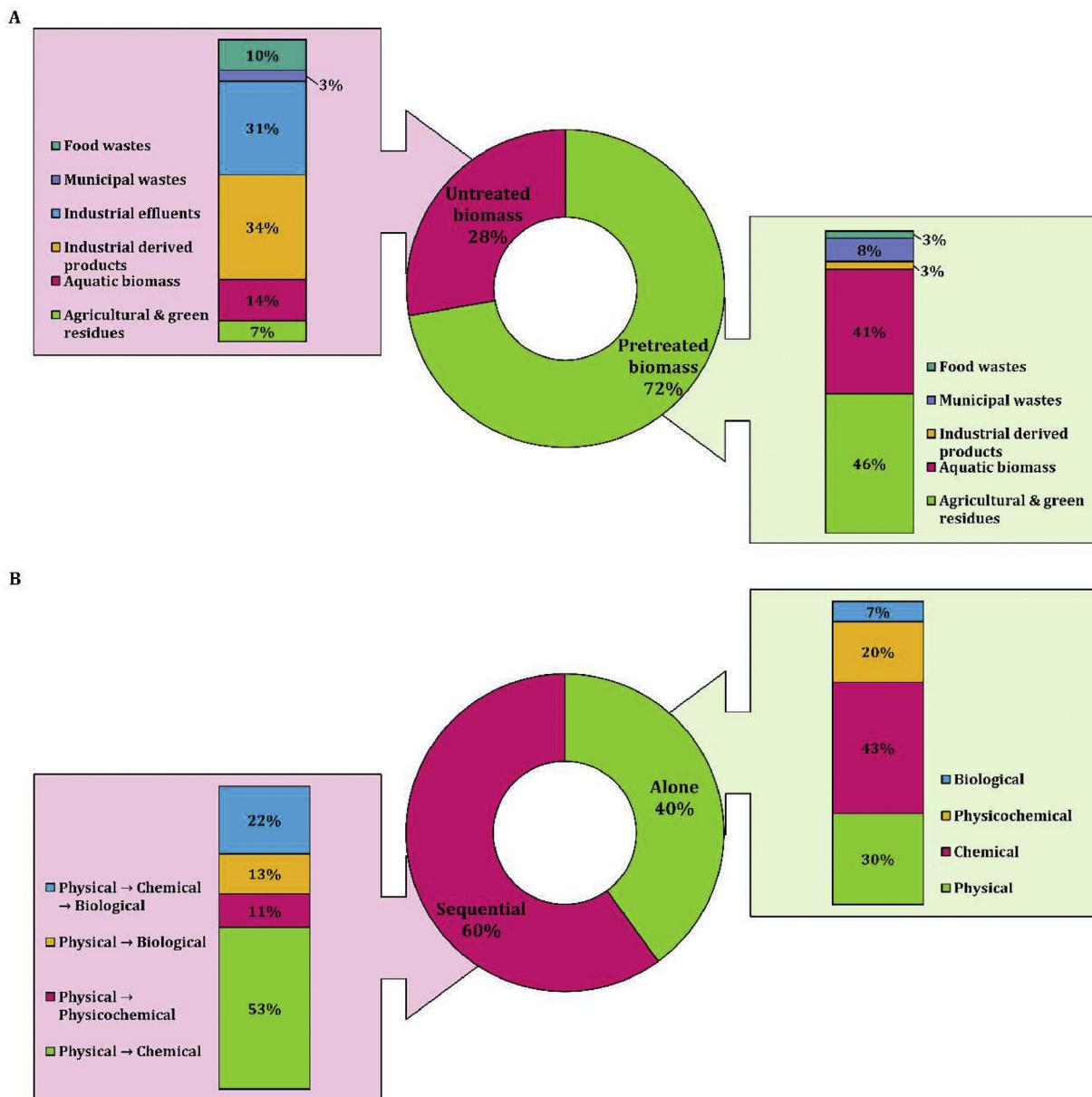


Fig. 4 – Feedstock pretreatments commonly used before dark fermentation. Untreated and pretreated biomass (A). Single and sequential pretreatments (B).

(Fig. 7D), G₂ includes studies with values mainly between 1 and 172 mL H₂/g substrate, with an average of 68.1 ± 63.1 mL H₂/g substrate. The relation between YH₂ and S –considering G₂ data– is shown in Fig. S2B. A decreasing trend was observed in studies using biomass of Agricultural and green residues category as substrate. As previously reported, increasing substrate concentration may lead to a decrease in H₂ production [116]. However, the trend was not clear with those studies which used feedstocks of the Aquatic biomass category, since in this category were employed S values ranging 2.5–37.75 g/L, obtaining YH₂ > 90 mL H₂/g substrate. For the rest of the feedstocks, not enough data ($N \leq 2$) are available in the database to describe their trend. Additionally, the YH₂ changes are directly proportional to rH₂, as shown in Fig. S3B.

Chemometric analysis

The colourmap for Matrix X1 (Table S2) is shown in Fig. 8. The colourmap collects information from the dendrograms constructed with 24 objects (i.e., studied samples; Fig. S4A) in a space of 12 parameters (Table 3A, Fig. S4B). According to the HCA, three clusters are distinguished, described as follows.

Cluster A (Objects 1, 3, 6, 9, 11, 12, 17 and 22) is characterized by low S (4.8–16.3 g substrate/L), as well as low butyrate (BTA) concentration (0.16–3 g/L). The Sub-clusters A₁ and A₂ are unique due to high pH values (6.8–8.5) and high YH₂ values (>423 mL H₂/g substrate), respectively. The colourmap shows the singularity of Object 3 due to the lowest YH₂ (84.73 mL H₂/g substrate) as well as Object 11 due to the highest pH (8.5)

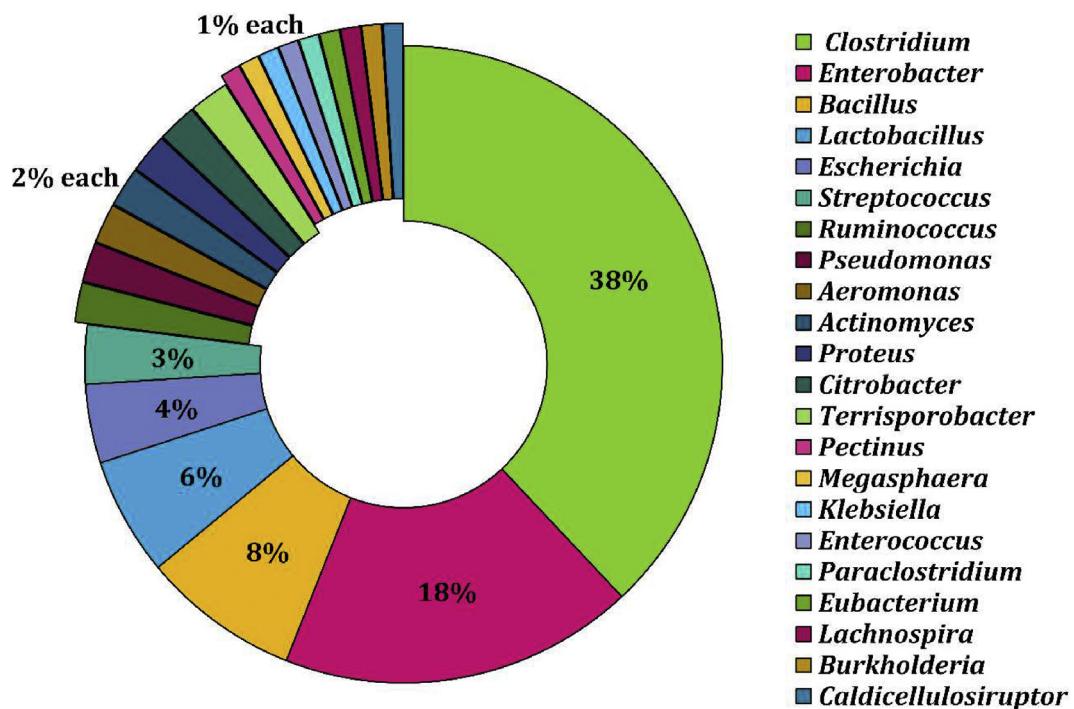


Fig. 5 – Microorganisms used or found in dark fermentation.

among all studied samples. Object 22 is distinguished by the lowest concentration of BTA (0.16 g/L).

Cluster B (Objects 2, 5, 7, 8, 13, 18 and 24) is identified by low YH₂ (41.4–282.7 mL H₂/g substrate). Sub-cluster B₁ is unique

due to the high concentration of BTA (1.71–6 g/L) in comparison with the rest of the Objects. The highest S value (59.2 g/L) is found in Object 8 with a relatively low pH (5.5). Objects 2 and 5 are differentiated by a high concentration of BTA, 6 and

Table 10 – Mixed and pure cultures used/defined in dark fermentation-bioreactors according to feedstock categories.

Feedstock category	Mixed culture		Pure culture
	Undefined	Defined	
Agricultural & green residues	<i>Clostridium</i> ^a <i>Clostridium/Enterobacter</i> ^b <i>Clostridium/Enterobacter/Terrisporobacter</i> ^c <i>Clostridium/Enterobacter/Lachnospira/Citrobacter</i> ^d <i>Ruminococcus</i> ^e <i>Clostridium</i> ^f <i>Clostridium/Enterobacter</i> ^g <i>Clostridium/Ruminococcus</i> ^h <i>Clostridium/Eubacterium</i> ⁱ <i>Clostridium/Bacillus/Lactobacillus</i> ^j <i>Clostridium/Enterobacter/Aeromonas/Bacillus</i> ^k <i>Clostridium/Bacillus/Terrisporobacter/Paraclostridium/Enterococcus/Actinomyces</i> ^l <i>Clostridium/Lactobacillus</i> ^m <i>Clostridium/Enterobacter</i> ⁿ <i>Clostridium/Enterobacter/Lachnospira/Citrobacter</i> ^d	<i>Clostridium/Bacillus</i> ^s <i>Clostridium/Citrobacter</i> ^t	<i>Clostridium</i> ^x <i>Enterobacter</i> ^y <i>Bacillus</i> ^z <i>Proteus</i> ^{ai}
Aquatic biomass	<i>Clostridium/Escherichia</i> ^u		<i>Clostridium</i> ^{bi} <i>Enterobacter</i> ^{ci} <i>Pseudomonas</i> ^{di} <i>Caldicellulosiruptor</i> ^{ei}
Industrial derived products			<i>Clostridium</i> ^{fi}
Industrial effluents		<i>Escherichia/Enterobacter</i> ^v	
Municipal Waste			
Food waste		<i>Enterobacter/Bacillus/Proteus</i> ^w	

^a[160,211], ^b[163,219,338], ^c[341], ^d[334], ^e[361], ^f[44,135,212,362], ^g[48], ^h[47], ⁱ[115], ^j[138,139], ^k[273], ^l[287], ^m[350], ⁿ[58], ^o[112], ^p[111], ^q[109], ^r[164], ^s[134], ^t[288], ^u[220], ^v[113], ^w[284], ^x[140,161,162,270,280,337], ^y[116,285,340], ^z[205], ^{ai}[286], ^{bi}[343,346,347], ^{ci}[279,344,345], ^{di}[349], ^{ei}[215], ^{fi}[204].

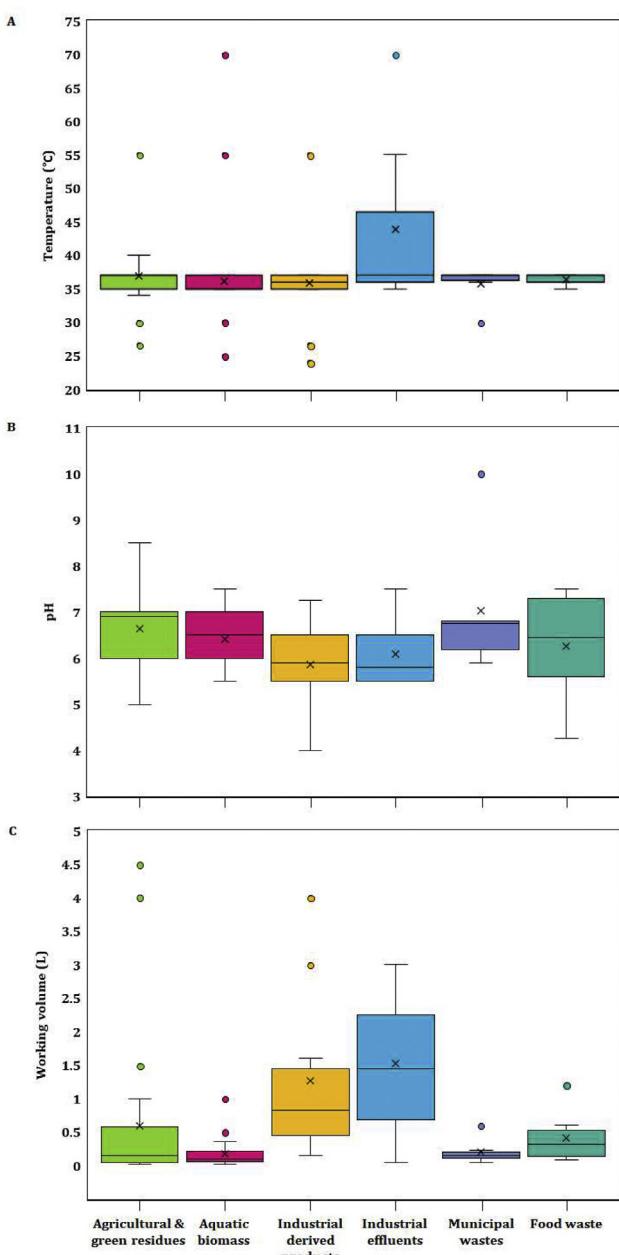


Fig. 6 – Temperature (A), pH (B) and working volume (C) used for hydrogen production via dark fermentation according to the feedstock employed.

5.60 g/L, respectively. Objects 18 and 24 collected in Sub-cluster B₂ are characterized by low pH values, 4 and 4.25, respectively.

Cluster C comprises Objects 4, 16, 19, 20 and 21. These Objects are particular due to the relatively high V_w (1.5–3 L) and concentration of lactate (LA, 1.49–7 g/L). Sub-cluster C₁ (objects 4, 20 and 21) is additionally characterized by relatively high T (55–70 °C). Object 21 reports the highest temperature (70 °C) among all studied samples. The singularity of Sub-cluster C₂, with Objects 16 and 19, is due to high V_w, 1.6 and 3 L, respectively. Further, the uniqueness of Object 16 could be observed, mainly due to the lowest T and YH₂ –24 °C and 99.73 mL H₂/g substrate – and relatively low value of pH (5.1) in comparison

with the rest of the Objects. Additionally, Objects 16 and 20 are identified by the highest concentration of LA (7 g/L each).

Four of the studied Objects are non-grouped (Objects 10, 14, 15 and 23). Non-grouped Objects 15 and 14 exhibit the highest rH₂ (1020 mL H₂/L·h) and concentration of acetic acid (AcOH), 45 g/L, respectively. Moreover, the uniqueness of Object 10 is caused by the highest concentration of formate (FA, 1.45 g/L), while Object 23 is singular with the highest concentration of ethanol (EtOH, 10.17 g/L) and propionate (EtCO₂, 2.69 g/L).

The colourmap for the data organized in Matrix X2 (Table S3) is presented in Fig. 9. The studied objects were collected into three main clusters (Fig. S5A). The parameters in the space of the studied objects were collected into three classes (see Fig. S5B). The distinguished clusters are described below.

Cluster D (objects 2, 3, 5–9, 12, 13, 15–17 and 21) is characterized by low H₂ac (107.5–1079 mL H₂/L) and YH₂ (4.6–77.2 mL H₂/g substrate). Sub-cluster D₁ (objects 2, 5, 7, 8, 13 and 17) exhibits a relatively high pH (6.5–7) in comparison with the rest of the Objects. The Objects collected in Sub-cluster D₂ were identified by the lowest YH₂ (8.96–55 mL H₂/g substrate) among all studied Objects. Object 9 of Sub-cluster D₂ exhibits the highest concentration of AcOH (4.95 g/L). The Objects in Sub-cluster D₃ exhibit the highest S (40–43 g/L). Object 16 is unique in Cluster D due to the highest T (70 °C) among all studied Objects.

Cluster E (Objects 1, 10, 19 and 20) is identified by relatively high YH₂ (168.6–219.67 mL H₂/g substrate) compared with the rest of the Objects. Object 1 within sub-cluster E₁ is singular by the highest YH₂ (219.67 mL H₂/g substrate) and the lowest value of pH (5.5) among all Objects. Object 19, non-clustered within Sub-cluster E₁, is characterized by the highest concentration of EtCO₂ (1.14 g/L).

Objects 4, 11, 14 and 18 were grouped in Cluster F, due to their high AcOH and BTA concentrations (2–8.83 g/L and 2.33–13.22 g/L, respectively). Sub-cluster F₁ is additionally distinguished by a high concentration of EtOH (0.42–0.47 g/L). The highest concentration of EtOH is observed in Object 14. The highest rH₂ (162.8 mL H₂/L·h) among all Objects was exhibited by Object 4. Object 11 is differentiated by the highest concentrations of AcOH (8.83 g/L) and BTA (13.22 g/L). Object 18 exhibits the highest V_w (2 L) and H₂ac (4862 mL H₂/L) among all studied Objects.

The HCA highlights the role that both pH and temperature play in DF performance. High rH₂ values are related to both $6 \leq \text{pH} \leq 6.8$ and $35^\circ\text{C} \leq \text{T} \leq 37^\circ\text{C}$ (see Objects 5 and 13 of Sub-cluster B₁, no-grouped Object 15 of Matrix X1, Object 5 of Sub-cluster D₁, objects 4 and 14 of Cluster F). Whereas low pH is related to low rH₂ as showed by Sub-cluster B₂. In addition, high YH₂ are related to mesophilic conditions as well as $5.5 \leq \text{pH} \leq 7.5$ (see Sub-cluster A₂ and Cluster E). Although thermophilic conditions may lead to high YH₂ values, an appropriate combination of T and pH should be used. Otherwise, YH₂ might decrease, as shown in Sub-cluster C₁, as well as in Objects 6 and 16 of Cluster D. Further, the HCA confirms that S significantly affects YH₂. This can be observed in both Sub-cluster A₂ and Cluster E, which obtain high values of YH₂ at low levels of S. High levels of S might lead to the accumulation of VFAs, as occurs in Sub-clusters B₁ and D₃, and object 18 of Cluster F as well. With the accumulation of VFAs, the pH decreases and the oxidation-reduction potential increases.

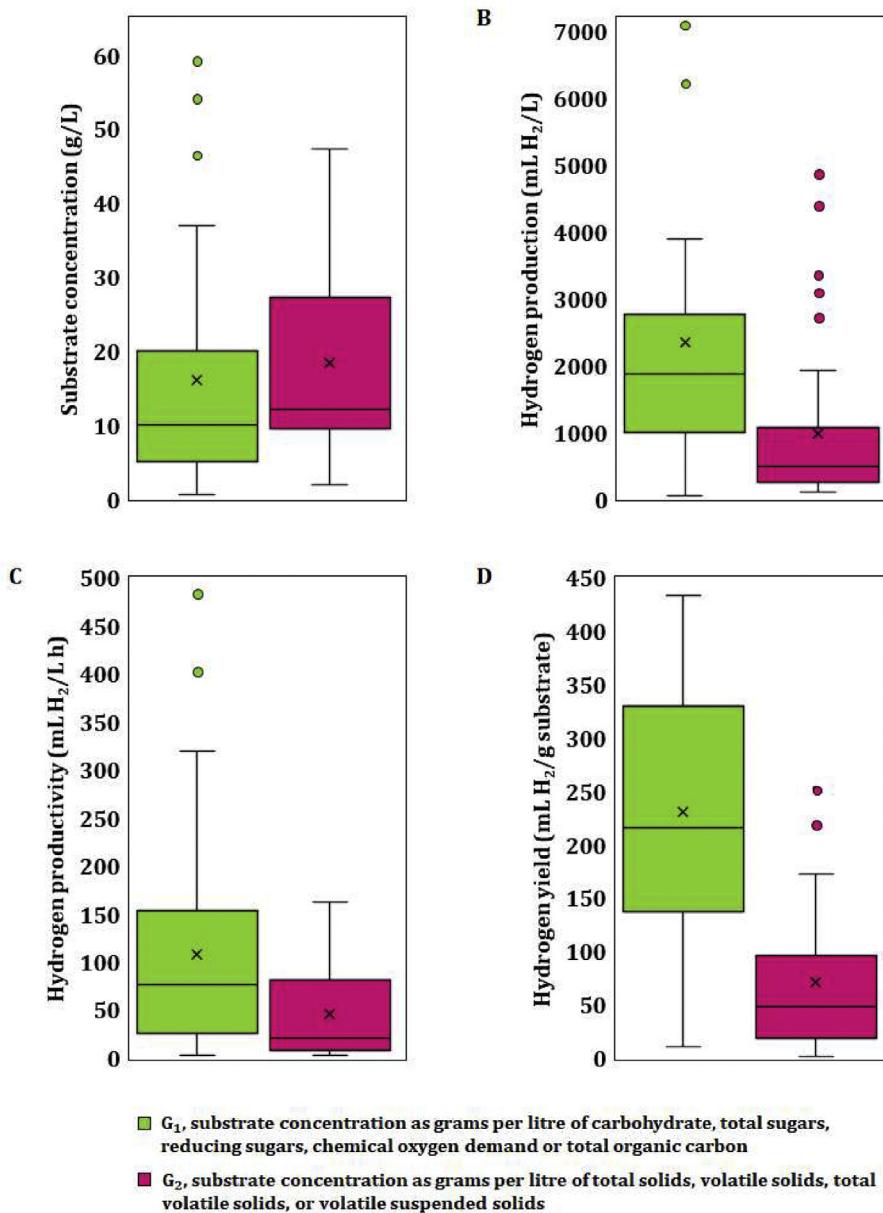


Fig. 7 – Dark fermentation performance. Substrate concentration (A), hydrogen production (B), hydrogen productivity (C) and hydrogen yield (D) reported in studies from the database.

Additionally, the balance of NAD⁺/NADH is modified, thus decreasing metabolic activity and leading to enzymes inactivation involved in H₂ production [117,118]. Moreover, H₂ partial pressure may also be influenced by S, which is related to inhibitory effects on the performance of DF [119,120].

By-products of dark fermentation

The by-products of DF, shown in Fig. 10A, are a mixture of VFAs and solvents (Fig. 11). These fermentative metabolites are related to the operational conditions (T, pH, S) and starter culture, as explained in Section [Feedstock pretreatment](#)

[methods](#) and Section [Hydrogen-producing microorganisms](#). The most abundant by-products –with amounts >2 g/L– identified with the HCA were AcOH, LA, EtCO₂, BTA, and EtOH. AcOH, LA, BTA, and EtOH are metabolites associated with hydrogenic bacteria [83,121,122]. EtCO₂ can be a metabolite in some H₂-producing systems as well. However, propionic fermenters must be avoided in DF since they can consume H₂ and/or reduce equivalents [67,123]. Production of chemicals from biomass offers a promising opportunity to improve the economics and sustainability of an integrated biorefinery while reducing the dependence on fossil fuels. In the following sections, production performance and economy are discussed for main DF metabolites.

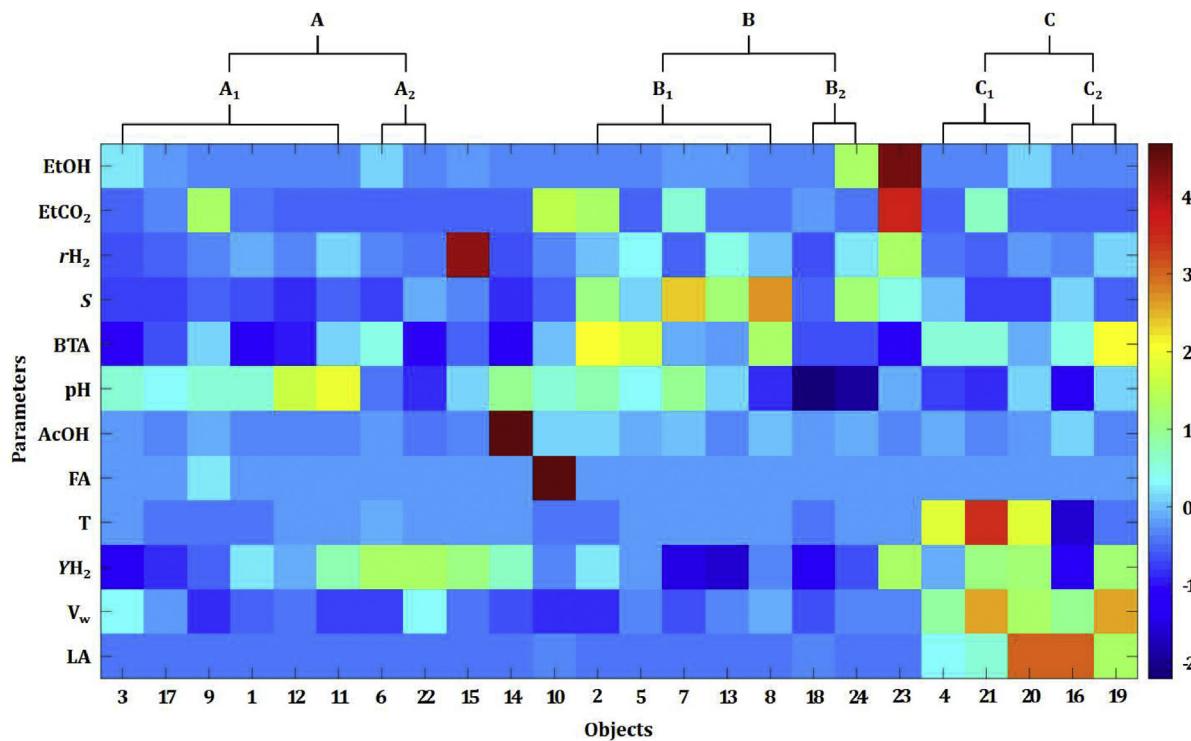


Fig. 8 – Colourmap of the studied data (Matrix X1) demonstrating the values of the measured parameters for measuring points.

Acetic acid

AcOH ($C_2H_4O_2$ or CH_3COOH) is one of the most important chemicals with increasing global demand (16–18 million tonnes in 2020) [129,130]. It is employed as a food preservative or flavouring agent in the food processing industry, and as

process solvent, or raw material in a large number of chemical processes (e.g., latex emulsion resins for paints, adhesives, textile finishing agents, cigarette filter tow, cellulosic plastic) [129,131]. Its global market size was estimated at USD 8.92 billion in 2019, with the Asia Pacific dominating the market with 62.0% of the global revenue [132]. Currently, AcOH is

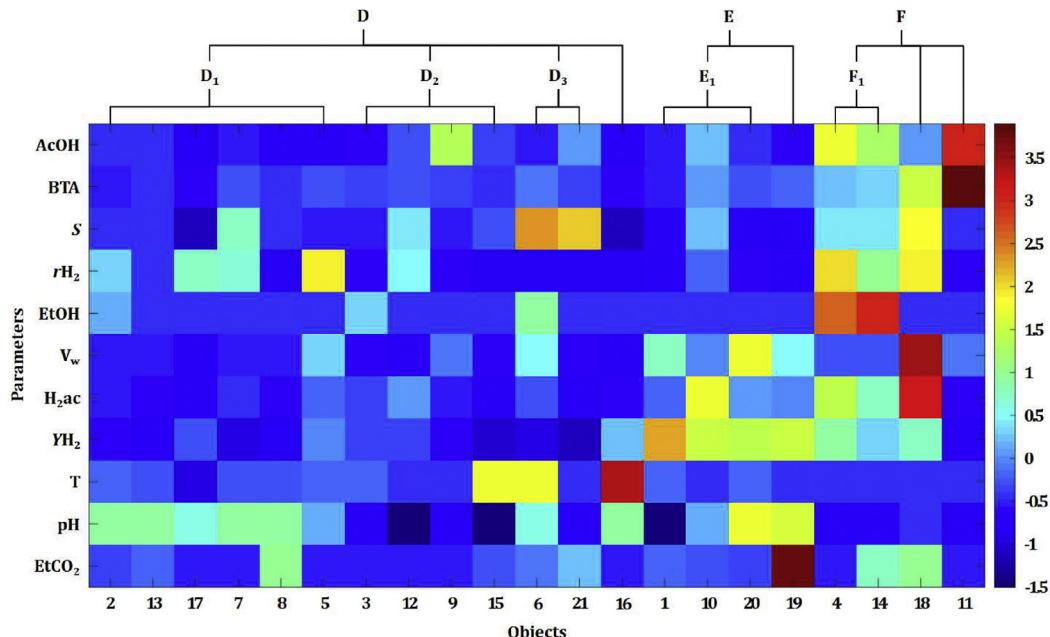


Fig. 9 – Colourmap of the studied data (Matrix X2) demonstrating the values of the measured parameters for measuring points.

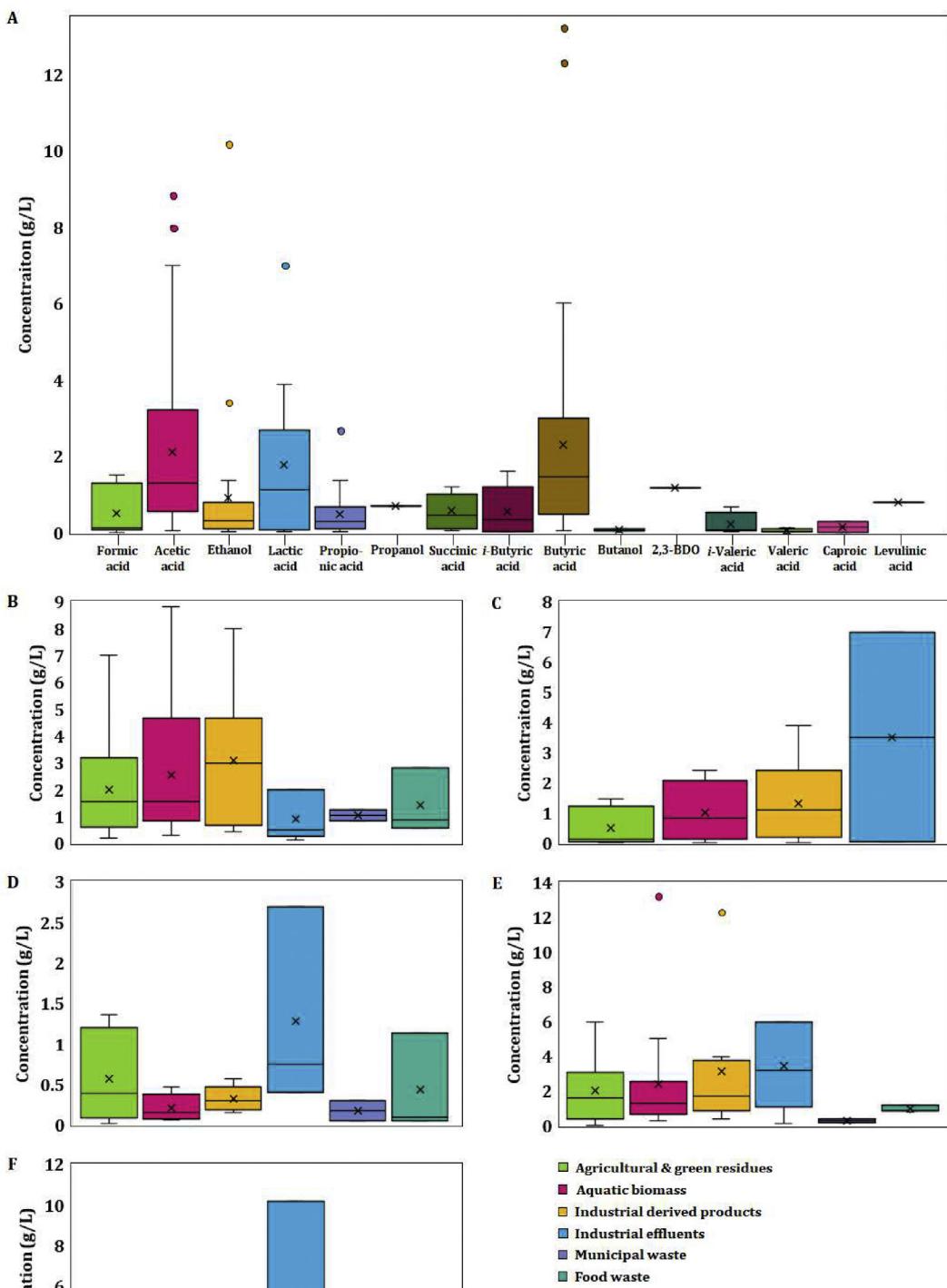


Fig. 10 – By-products generated during hydrogen production via dark fermentation (A). Acetic (B), lactic (C), propionic (D), butyric (E) acids, and ethanol (F) production as a function of feedstock employed.

mainly produced through carbonylation of methanol and oxidation of ethylene or acetaldehyde [131,133]. In this regard, production based on microbial fermentation is considered a clean alternative, but still with low productivities.

In this work, AcOH was produced in concentrations between 0.04 and 8.8 g/L, with an average amount of 2.1 g/L. According to the HCA, high AcOH concentrations seems to be associated with high S (Sub-clusters B₁ and D₃, Object 18 of

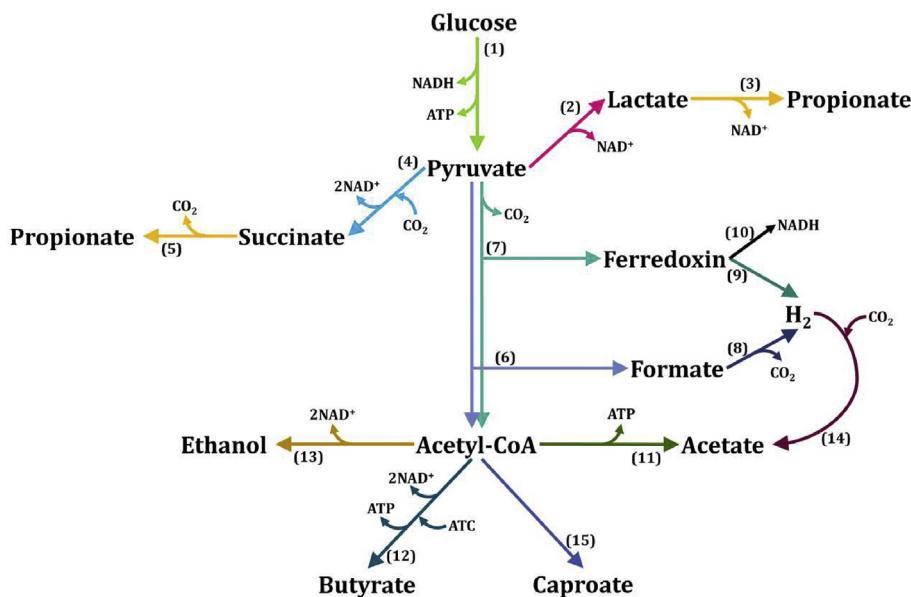


Fig. 11 – Main catabolic pathways in acidogenic glucose fermentation, adapted from Refs. [124–128]. Reaction (1) illustrates the formation of pyruvate from glucose. NADH produced [reaction (1)] should be reconverted to NAD⁺. One way is through the production of lactate from pyruvate [reaction (2)]. Propionic acid is also formed during glucose fermentation by the acrylate pathway [reaction (3)], in which extra NADH is transformed to NAD⁺. During the succinate pathway, reactions (4) and (5), 2 NADH can be reconverted. This pathway also consumes CO₂ for succinate synthesis. Another way to regulate glucose catabolism is via the production of acetyl-CoA by the pyruvate formate lyase pathway [reaction (6)] or the pyruvate dehydrogenase pathway [reaction (7)]. Formic acid [reaction (6)] is transformed by the formate-hydrogen lyase into H₂ and CO₂ [reaction (8)]. Reduced ferredoxin [reaction (7)] transfers electrons to hydrogenase to generate H₂ [reaction (9)]. NADH:ferredoxin reductase [reaction (10)] transfers electrons from reduced ferredoxin to NAD⁺ producing NADH. Acetic acid is produced from acetyl-CoA [reaction (11)] accompanied by the production of ATP. Acetic acid may also be produced via homoacetogenesis [reaction (14)], which consumes H₂ and CO₂. Butyric acid synthesis [reaction (12)] is performed through the condensation of acetyl-CoA and acetic acid. Ethanol production from acetyl-CoA [reaction (13)] is catalysed by the aldehyde dehydrogenase and the ethanol dehydrogenase. The combination of acetyl-CoA with butyryl-CoA leads to caproate [reaction (15)].

Cluster F) and thermophilic conditions (Sub-cluster C₁), as well as with low YH₂ (Object 9 of Sub-cluster D₂, Object 11 of Cluster F), as shown Figs. 8 and 9. The highest concentrations (≥ 7 g/L) of AcOH were produced using biomass from Agricultural and green residues, Aquatic biomass, and Industrial-derived products categories (Fig. 10B). Sugarcane bagasse, after submitted to physical/chemical/biological pretreatment, was used as feedstock for DF by a co-culture of *C. pasteurianum* and *B. subtilis*. The mixture of VFAs and solvents at the end of the fermentation period was dominated by AcOH (7 g/L), followed by BTA (1.8 g/L), succinate (1 g/L), and EtOH (0.4 g/L) [134]. Acid-hydrolysate of algal bloom biomass was utilized to perform DF using a microbial consortium dominated by *C. butyricum*, after 72 h the main by-products were AcOH (8.8 g/L) and BTA (13.2 g/L) [135]. The DF, using an undefined mixed culture, of cheese whey produced a mixture of VFAs conformed by AcOH (8 g/L), BTA (4 g/L), i-butyrate (0.77 g/L), and EtCO₂ (0.25 g/L) [136]. Other biomasses such as rice straw and rice husk of Agricultural and green residues category, as well as cyanobacteria and cordgrass of Aquatic biomass category, have been used as feedstock to perform DF obtaining AcOH as the main by-product in amounts of 4–6 g/L [137–140].

Recent research has been focusing on improving the production of AcOH by DF using both pure and mixed cultures.

Using glucose as substrate and seed sludge (thermally pre-treated, without bacterial phylotype identification) from an anaerobic reactor treating pig manure as inoculum, co-production of H₂ (13.39 mmol/d) and AcOH (1.74 mol/mol glucose) was achieved by controlling the headspace pressure at 20 kPa [141]. Further, the co-culture of *C. thermosaccharolyticum* and *C. thermocellum* using sweet sorghum stalks (dried and ground) as substrate was optimized to improve the co-production of H₂ and VFAs (AcOH and BTA) [142]. In addition, a two-step fermentation of sweet sorghum stalks using *C. thermosaccharolyticum* was proposed increasing H₂, AcOH, and BTA yields by 95%, 97%, and 143% compared with those obtained in a single step fermentation without any treatment [143]. Further, coffee silverskin (without pretreatment) was used as feedstock to perform DF (semi-batch operation). The indigenous microflora converted organic matter into H₂, obtaining AcOH as the main metabolite, while BTA, EtOH, and EtCO₂ were produced in lower amounts. After DF, the microflora was abundant in AcOH-producing *Enterococcus* (54.1%), followed by H₂-producing bacteria affiliated to *Enterobacteriaceae* (27.5%) and *Clostridium* (5.1%) [144]. Co-production of H₂ and AcOH may be improved by modification/optimization of operational conditions (e.g., T, S, feedstock, and inoculum) as well as feedstock pretreatment. Still, further investigation is

needed to make co-production H₂ and AcOH sustainable and competitive.

Lactic acid

LA (C₃H₆O₃ or CH₃CHOHCOOH) is a widely available organic acid in nature with applications in the food, chemical, cosmetic, and pharmaceutical industries. Due to its chemical properties, it can be used as a precursor of small (propylene glycol) or large (acrylic polymers) compounds. Additionally, it is employed as a monomer in the production of biodegradable and biocompatible polylactic acid, which is used as a raw material in packaging as well as fibres and foams [145–147]. The global LA market size was estimated at USD 3.1 billion in 2019, is dominated by North America with a share of 45.2% [148]. Most commercial production of LA is by microbial fermentation of carbohydrates, its price reaching around 3.0–4.0 USD/kg and is expected that its demand will reach ~2.0 million tonnes in 2025 [149].

LA was produced in studies employing biomass from the following categories as feedstock: Agricultural and green residues (0.05–1.49 g/L), Aquatic biomass (0.02–2.4 g/L), Industrial-derived products (0.02–7 g/L), and Industrial effluents (0.05–7 g/L) (Fig. 10C). HCA established that studies grouped in Cluster C are characterized by high LA concentrations. These studies employed 5.1 ≤ pH ≤ 6.5. Further, LA as the main metabolite was found using seaweed (2.4 g/L, S: 24 g TS/L [46]; 0.55 g/L, S: 10 g VS/L [47]), cheese whey (7 g/L, S: 20 g lactose/L [150]), wheat starch (3.89 g/L, S: 3.6 g COD/L [151]), and sugarcane vinasse (7 g/L, S: 5.02 g carbohydrate/L [110]) as substrate. However, reduced end products such as LA must be avoided during DF to maximise YH₂ values, since its presence represent H₂ that was not released as a gas [66,120].

Propionic acid

EtCO₂ (C₃H₆O₂ or CH₃CH₂COOH) and its salts (calcium, sodium, and potassium) are largely used as preservatives in processed foods (e.g., fungistatic agent in bread and bakery products) and animal feed. It is also employed in the manufacturing of cellulose acetate propionate and vitamin E, as well as an esterifying agent in thermoplastics production and flavours and perfume bases manufacture. The global EtCO₂ production was estimated at approximately 450,000 tonnes per year with 2–3 USD/kg as selling price [152]. EtCO₂ is mainly produced by petrochemical processes such as oxidation of propanol or propanal, hydrolysis of esters, and hydrocarboxylation of ethylene [152–154].

EtCO₂ was identified in almost 40% of the studies in the database in concentrations from 0.02 to 2.7 g/L, with an average of 0.5 g/L (Fig. 10D). Although EtCO₂ may be part of DF by-products, is not the metabolite target. The HCA showed that mesophilic conditions, 6.3 ≤ pH ≤ 7.4, and 5 g/L ≤ S ≤ 24 g/L may promote mixtures of VFAs with BTA or EtOH as the main metabolite accompanied by certain amounts of EtCO₂ (1.1–2.7 g/L), as occurs in Objects 2, 9, 10, and 23 from Matrix X1 and Object 19 of Cluster E. VFAs generation was influenced by fermentation conditions, such as T. It has been demonstrated that VFAs production at thermophilic conditions is lower (40%) than mesophilic conditions [155]. Likewise,

optimal pH for the production of a specific VFA is highly dependent on the type of feedstock employed [156]. EtCO₂ production from wastewater is favoured at a pH of 4–4.5, whereas for AcOH and BTA, a pH of 6–6.5 is desired. Using cheese whey, modification of pH from 5.25 to 6 leads to an increase in EtCO₂ production with low amounts of BTA and AcOH. Production of AcOH and EtCO₂ is promoted instead of BTA by pH changes from 6 to 8 in the fermentation of a glucose-rich substrate. This behaviour might be due to the shift in the dominant microbial populations due to pH changes [155,156]. However, high YH₂ values are usually associated with BTA production and low production of EtCO₂ and reduced end products (e.g., alcohols, LA) [120].

Butyric acid

BTA (C₄H₈O₂ or CH₃CH₂CH₂COOH) and its derivates have a wide range of applications. It can be used as a precursor in the production of CAB (cellulose acetate butyrate), intensifier butter-like notes in food flavours, additive to fibres for heat and sunlight resistance enhancement, enhancer of fruit fragrance. Also, it is used in the treatment of hemoglobinopathies, cancer, and gastrointestinal diseases. Nowadays, BTA is produced through chemical synthesis exclusively, with a worldwide market of over 80,000 tonnes per year at an approximate price of 1.8 USD/kg [157–159]. Biotechnological production of BTA is not commercially competitive, because of its low production rate and low concentration in the fermentation broth. However, food and pharmaceutical manufacturers prefer food additives or pharmaceutical products produced biologically.

BTA was found in research articles using biomass from Agricultural and green residues (0.04–6 g/L), Aquatic biomass (0.03–13.2 g/L), Industrial derived products (0.4–13.2 g/L), Industrial effluents (0.16–6 g/L), Municipal wastes (0.17–0.4 g/L), and Food wastes (0.85–1.17 g/L), as shows Fig. 10E. The average amount of BTA observed was 2.3 g/L. According to the HCA, high amounts of BTA were related to high S (Sub-clusters B₁ and D₃, Object 18 of Cluster F) and relatively low YH₂ (Objects 11 and 14 of Cluster F). Additionally, BTA production is usually accompanied by AcOH (Sub-cluster B₁, Clusters C and F). Clostridium strains have been recognized by achieving high production rates and high final concentrations of BTA. As a mixed or pure culture, Clostridium used feedstocks such as empty fruit brunch of oil palm [160], carob pulp [161], corn stalk [162], rice husk [163], algal bloom [135], co-culture of tequila vinasses and nixtamalization wastewater [109], and tequila vinasses [164], to produce BTA as the main by-product of DF in amounts of approximately 5–13 g/L. Also, using seaweed and wheat bran was produced BTA in high amounts (5–12 g/L) but information of the microbial community employed is not provided [165,166].

Although H₂ production is associated with the production of AcOH and BTA, high acid concentration may reduce H₂ production by acidification of the media, as well as bacterial metabolism inhibition [67,101]. Nevertheless, controlling the buffering system (NaOH + CaCO₃), BTA production was enhanced (almost 3-fold) during DF using food waste as substrate [167]. Another strategy adopted was to increase the initial organic load (>26.2 g VS/L, food waste), leading to ~5-fold increments of BTA production [168]. In addition,

optimization of the conditions of pH (7) and T (35 °C) –using 80 or 100 g VS/L of microalgae as substrate–, generates high yields of H₂ (22 mL H₂/g VS) and BTA (0.05 g/g VS) [169]. The combination of strategies (e. g., fed-batch fermentation, repeated fermentation, cell immobilization, co-culture or mixed culture, metabolic engineering) with pH-control can be also an alternative for highly efficient BTA production [158].

Ethanol

EtOH (C₂H₆O or CH₃CH₂OH), is one of the organic chemicals most used in industrial and consumer products. Moreover, its physicochemical properties make it a suitable engine fuel. EtOH is currently commercialized as a fuel oxygenator or biofuel to reduce environmental impacts related to fossil fuels, as well as to improve their performance since its octane number is higher (106–110) than gasoline's (91–96) [170,171]. EtOH (biofuel) production reached 110 billion L globally in 2018 and is anticipated a 20% increase by 2024 [172].

EtOH concentration average of 0.9 g/L was found in the research articles included in the database, as shown in Fig. 10F. In studies using biomass from Agriculture and green residues, Aquatic biomass, Industrial derived products, and Municipal waste categories, EtOH was identified in amounts <1.5 g/L. Using Industrial effluents and Food wastes as feedstock, EtOH is the main metabolite and appears in concentrations of 10 g/L [113] and 3.4 g/L [173], respectively. Although EtOH is not the target product in DF, EtOH production seems to be favoured at mesophilic conditions and pH approximately of 4.2–6.3 (Object 24 of Sub-cluster B₂, non-clustered Object 23 of Matrix X1, Objects 4 and 14 of Cluster F). Further, EtOH production is not linked to VFAs production, such as BTA and AcOH (Sub-clusters A₁, B₁, Cluster C, Objects 11 and 18 of Cluster F). This is because mixed cultures used in DF are dominated by strains of *Clostridium* in which –under mesophilic and/or thermophilic conditions– the metabolic flux favours the AcOH and BTA production instead of EtOH [109,111,164]. The highest EtOH production (10.17 g/L) was reported employing a co-culture of *E. coli* and *E. cloacae* as starter culture and crude glycerol as substrate [113]. Both *Escherichia* and *Enterobacter* strains produce H₂ and EtOH from glycerol under anaerobic conditions [174–176].

EtOH concentration must be >4% (w/w) for a profitable separation using distillation [177]. Considering the titters obtained in DF (average of 0.9 g/L, according to database), EtOH production by mixed-cultures is neither economic nor energetically competitive compared with corn- and sugarcane-based EtOH [178].

Challenges for industrial production of bio-based chemicals

Bio-based chemicals production is an alternative to the renewable production of chemicals building blocks. Notwithstanding, to be competitive with petrochemical processes, microbial conversions must achieve high productivities and yields. Therefore, some issues must be addressed before establishing microbial production on a commercial scale. To achieve a profitable production of VFAs (e.g., AcOH, BTA, LA, EtCO₂), titters of 50–100 g/L, production rates of 1–3 g/L·h, and yields >0.5 g/g are required [159,179]. Furthermore, the

microorganisms (mixed or pure cultures) should be capable to tolerate these acids at such high concentrations.

The main limitation of VFAs recovery from DF effluents is the extraction/purification step. Although these operations represent the major contributor to the VFAs production cost [180], low-cost purification processes have not been developed yet for AcOH, BTA and EtCO₂ [178]. The recovery of individual VFAs is even more difficult than of VFAs mixtures [181]. So far, technologies used for VFAs recovery after the fermentation stage from broths include gas stripping with absorption [182,183], adsorption [184,185], electrodialysis [186,187], solvent extraction [188,189], nanofiltration [190], reverse osmosis [191], and membrane contactors [192]. However, in-situ recovery of VFAs, which can either be carried out continuously or intermittently during fermentation [193] can also prevent product-inhibitory effects as well as VFAs consumption during internal conversion reactions [181,193,194]. The in-situ recovery of VFAs can also increase VFAs production rates [195], extraction yields [196], extraction efficiency [197,198], as well as the reduction of carbon footprint [199].

Further research is required to develop profitable production and recovery methods. Besides, a deeper understanding of microbial communities and their interactions with VFAs production pathways will be fundamental to achieving profitability [181,200].

Dark fermentation in biorefineries

Despite being a renewable and clean energy source, H₂ via DF has relatively low energy conversion efficiency (ECE) which restricts its commercial application. However, DF effluents contain abundant residual energy in the form of VFAs that can be converted into methane (CH₄), biodiesel, biopolymers (poly-hydroxy alkanoates, PHAs) or even more H₂ [201–205]. To be sustainable, DF must be integrated into biorefining strategies with bioenergy or value-added co-products as their outputs (Fig. 2A).

A biorefinery scheme including a DF stage followed by anaerobic digestion (AD) stage might be an alternative to improve energy balance. During the AD stage, residual soluble organic matter and VFAs from the DF stage can be used by methanogenic archaea (viz *Methanosarcina* sp. and *Methanoculleus* sp.) to produce CH₄ [206]. The final product of this sequential two-stage process is called bio-hythane (H₂ + CH₄), with an overall fermentation time of 13–18 days. Bio-hythane production in a two-stage process can improve energy recovery and reduce fermentation time. Further, the separation of AD from DF provides good control of microbial communities with different functions [207,208]. According to the database, bio-hythane production has been tested using biomass from Agricultural and green residues, Aquatic biomass, and Industrial derived products categories. A system combining DF and AD employing *Platanus orientalis* leaves improved 6.18-fold ECE compared to a single DF stage [209]. Using sugarcane tops in a similar system, an energy recovery of 7.07 MJ/kg VS was achieved [210]. Utilizing sugarcane bagasse, the energy recovery was improved by coupling DF with AD (8400 kJ/kg VS, 44.8% of energy recovery) compared with a single DF stage (4600 kJ/kg VS, 24.5% of energy recovery) [211]. Biomass from microalgae [*Chlorella* sp., microalgae

consortium (*Scenedesmus*, *Keratococcus*, *Oscillatoria*]), seaweed (*Sargassum* sp.), algal bloom (*Microcystis*), water hyacinth (*Eichhornia crassipes*), and cordgrass (*Spartina anglica*) were used in two-stage bio-hythane production processes, obtaining an ECE between 20% and 75%, and an energy recovery up to 16 kJ/g VS [115,135,139,212–215]. Wheat bran seems to be a suitable feedstock for bio-hythane production in two-stage processes with energy recovery of 9.0 MJ/kg VS [165]. Since H₂ is a carbon-free fuel, its combination with CH₄ may contribute to reducing CO₂ and NO_x emissions to the atmosphere [216]. Despite several advantages of bio-hythane production, challenges related to metabolic pathways, reactor configuration, recycling of digestate, and physicochemical parameters must be addressed before scaling up for commercial production [202,217]. Further, an economic assessment of the two-stage process is also necessary before establishing full-scale plants.

VFAs produced during DF can be utilized for additional H₂ production. Under anoxygenic conditions, photosynthetic purple non-sulphur bacteria (PNS)—such as *Rhodopseudomonas palustris*, *Rhodobacter sulfidophilus*, *R. capsulatus*—can metabolize organic acids (e.g., acetate, butyrate, succinate, lactate) and produce H₂ and CO₂ using light as an energy source [218]. Effluents (acetate and butyrate) from DF of cornstalk were used to improve H₂ production through integration of photo fermentation (PF) by *R. capsulatus*, increasing the yield 1.5-fold compared with a single DF stage [219]. The two-stages DF by *E. coli* and *C. acetobutylicum* and PF by *R. capsulatus* produced in total 5.9 mol H₂/mole of reducing sugars from cyanobacterium *Nostoc commune* biomass which is approximately 2.3-fold that the obtained in the single-stage DF [220]. *Chlorella* sp. biomass was used as substrate for DF, obtaining 0.51 kJ/g VS. An energy recovery of 1.86 kJ/g VS was obtained by coupling it with PF [221]. *Arthrosphaera platensis* biomass was used to produce H₂ via DF with an ER of 1.03 kJ/g VS. After coupling it to PF, the energy recovery was increased to 4.63 kJ/g VS [138]. The combination of DF and PF seems a promising strategy for H₂ production since integrated systems may improve the H₂ yields and energy recovery. However, the theoretical H₂ yield (12 mol/mol glucose) of the integrated system has not been achieved yet [222]. Further, the light requirement and light penetration in PF is a challenging task at a large scale. These limitations can be addressed by DF effluents dilution. However, this intermediate step will increase CAPEX [223]. Despite VFAs consumption in the coupled stage, a considerable amount remains in the effluent from the coupled process. Thus, this represents a potential to further extend the two-stage process with an AD stage [138,224].

Another way to convert DF end products into H₂ is with microbial electrolysis cells (MEC). In MEC, organic substrates such as acetate are oxidised by microorganisms at the anode generating CO₂, protons, and electrons. Protons move to the cathode and its reduction to H₂ is driven by the addition of small voltage to the system [225]. The integration of DF with MEC has been recognized as a promising method to convert biomass into H₂. Integrated systems increased H₂ yields—using feedstock such as POME, vinasses, sugar beet juice—compared with a single DF stage system [226–229]. However, using fermentation effluents as substrate, the H₂ production rate can be decreased

and a substantial amount of methane can be produced [230]. Limitations such as low energy efficiencies, competing reactions (i.e., methanogenesis), growth of H₂ scavengers, among other factors, must be avoided before increasing the capacity of MECs to industrial scales [231]. Therefore, further research is required for integrating MEC technology with DF, considering techno-economic and sustainability studies.

VFAs in DF effluents can be harnessed for lipid production. Microbial lipids (single cell oil) are produced by oleaginous microorganisms such as yeast, bacteria, fungi, and microalgae from carbohydrates, hydrocarbons, and crude oils [232]. The general pathway of lipid synthesis from glucose involves its conversion to acetate and then its channelization to lipogenesis. However, some oleaginous microorganisms can use VFAs as the sole carbon source to accumulate lipids [233,234]. Further, DF effluents containing VFAs have been used to produce single-cell oil. Cornstalk was used to produce H₂ and lipid (algal lipid viz *Scenedesmus* sp.) in a two-stage process, the ECE increased from 5.78% to 16.96% compared with a single-stage process [235]. Duckweed biomass was used as feedstock for DF and *C. saccharophila* cultivation. As a result, microalgal growth and lipid production were promoted by using DF effluents as feedstock [94]. Effluents from DF of molasses were also employed as feedstock for lipid production. Coupling DF with the cultivation of *Scenedesmus* sp., 97.3% additional energy was produced compared with DF alone [236]. DF coupled with lipid production by *Rhodotorula minuta* improved the energy recovery as compared with a single-stage process [204]. Also, the ECE was enhanced from 10% to 24% using DF coupled with algal lipid production using food waste as feedstock [27]. Single-cell oil can be employed for biodiesel production. However, its application as feedstock depends, although not exclusively, on production costs. This gap can be addressed by reducing fermentation and downstream processing costs, as well as increasing microbial lipid productivity [237,238].

Emerging research is focusing on the use of DF residues to produce polyhydroxyalkanoates (PHAs). PHAs are biopolymers synthesized by microorganisms as lipid inclusions for energy storage in granular forms within the cellular structure [239,240]. Microorganisms capable to produce PHAs include, but not exclusively, *P. resinovorans*, *P. aeruginosa*, *P. putida*, *P. fluorescence*, *B. cereus*, and *Lysinibacillus sphaericus* [241]. The VFAs in DF effluents can act as a carbon source for microbial growth as well as precursors for biopolymers production (acetate for hydroxybutyrate, propionate for hydroxylvalerate, butyrate for hydroxyhexanoate) [239]. Renewable feedstock such as wastes from dairy industries [242], hydrolysed polyacrylamide-containing wastewaters [77], giant cane biomass [243], has been used in a system combining DF and PHAs production, obtaining approximately 1.4–2 mol H₂/mol sugars and 54–62 g PHA/g VSS. Coupling dark- and photo-fermentation and PHAs production have been tested as well. For example, rice straw hydrolysate was used for simultaneous H₂ and PHAs production combining DF by *B. cereus* and PF by *R. rutila*, obtaining approximately 1.6–1.8 mol H₂/mol sugars and 10–19 g/L PHAs [205]. H₂ is a clean and renewable energy source that may substitute fossil fuels, and PHAs are

biopolymers that can replace conventional petroleum-derived plastics. However, PHAs production costs are high depending on the type of carbon source, process productivity, production yields, fermentation cost, and downstream processing [244,245]. These challenges must be addressed to develop a commercial-scale two-stage process coupling DF and PHAs production.

An alternative for scaling-up H₂ production is solid-state fermentation (SSF) [246]. SSF is characterized by low water requirements, smaller reactor sizes, high TS contents (>15%), and high organic loading rates. However, performing DF using high TS may lead to low YH₂. H₂ production by SSF using microalgae as substrate has already achieved YH₂ < 20 mL H₂/g VS [247,248]. Rice husk was also subjected to SSF with a co-culture of *C. termitidis* and *C. intestinalis* (5:1) at 37 °C and 30 rpm. The YH₂ was 5.9 mL H₂/g substrate [249]. Further, ground wheat was used with *C. acetobutylicum* at mesophilic conditions achieving 63 mL H₂/g starch [250]. During SSF, the availability of water decreases due to its adsorption onto the biomass, leading to higher concentration of inhibitory compounds [246]. Moreover, high TS content is related to low mass transfer rates, which may induce unfavourable conditions to biological reactions [246]. Consequently, further studies are required to deeper understand H₂ production via SSF.

Concluding remarks

H₂ production from biomass via DF has been extensively studied. However, going from laboratory/pilot-scale to sustainable large-scale production envisages several challenges. A major hurdle is the low H₂ yield compared with the theoretical maximum. Besides, DF produces a stream rich in VFAs, which must be treated before disposal. However, this VFAs stream may be recovered by downstream processing for producing value-added products, methane, lipids, biopolymers, or even more H₂. Although the literature offers some solutions to address these gaps, their technology readiness level is still low. Techno-economic analyses, sustainability analyses, as well as life cycle assessments may help to establish the economic and environmental feasibility of industrial-scale designs.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2022.02.106>.

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