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Review Article

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

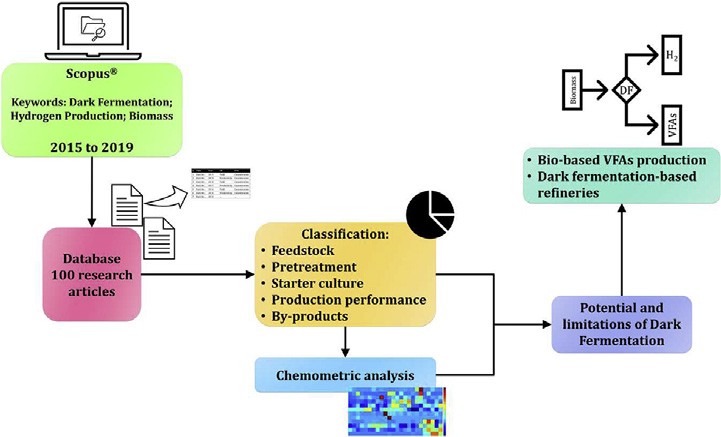
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## h i g h l i g h t s g r a p h i c a l a b s t r a c t

* Meta-analysis of research on H2

and by-products production using dark fermentation.

* Clusters created based on feed-

stock, process conditions and productivity.

* Review of production strategies

highlighting pros and cons.

* Discussion of challenges to inte- grating DF in large-scale bio- refining schemes.

## a r t i c l e i n f o

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## a b s t r a c t

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 microor- ganisms 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). Agri- cultural 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 ≤ pH ≤ 6.8 and 35 ◦C ≤ T ≤ 37 ◦C and H2 high yield to 5.5 ≤ pH ≤ 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 prog- ress has been based on the use of fossil fuels, causing the increase of carbon dioxide (CO2) 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 human- kind [[1](#_bookmark33),[2](#_bookmark34)].

Biomass is one of the major renewable sources of sus- tainable energy that can be efficiently stored in energy car- riers, such as methane, hydrogen, ethanol, and biodiesel [[3](#_bookmark35)]. Hydrogen (H2) is considered one of the most promising alter- natives 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 H2 is equivalent to the energy of 2.7 kg of petrol/gasoline or 6 kg of methanol [[4](#_bookmark36),[5](#_bookmark37)]. Furthermore, H2 is the cleanest fuel because its combustion releases only water and energy, with neither pollutants nor greenhouse gas

emissions [[6](#_bookmark38),[7](#_bookmark39)]. Biomass conversion into H2 can be achieved thermochemically [*e*.*g*., gasification (500e1400 ◦C), pyrolysis

(300e1000 ◦C), combustion (650e1000 ◦C), liquefaction (200e300 ◦C)], and biologically (*e*.*g*., biophotolysis, photo- fermentation, dark fermentation) [[8](#_bookmark40)e[12](#_bookmark40)]. However, thermo- chemical processes are related to high equipment costs (CAPEX) with large energy requirements [[13](#_bookmark41),[14](#_bookmark42)]. Besides, they can generate particulate matters and tar that affect the envi- ronment and human health [[15](#_bookmark43)]. Biological processes, in contrast, employ mild reaction conditions (30e80 ◦C at at-

mospheric pressure) with simultaneous H2 production and waste recycling [[16](#_bookmark44)]. Among these biological alternatives, dark fermentation (DF) is a well-understood method with high H2 production rates, and without light requirements [[4](#_bookmark36),[5](#_bookmark37),[17](#_bookmark45)].

H2 e*via* DFe is produced by obligate anaerobic or faculta- tive 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. H2 is produced when an electron is transferred to the proton. Biomass is converted into H2 mainly *via* the acetate and butyrate pathways [[18](#_bookmark46),[19](#_bookmark47)]. The maximum H2 yield with the acetate pathway is 4 mol H2/mol glucose consumed. If the substrate is a pentose (*e.g.*, xylose, arabinose), 3.33 mol H2/mol pentose are obtained. This is approximately equivalent to

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588.5 mL H2/g sugar[1](#_bookmark5) or 550 mL H2/g COD.[2](#_bookmark6) 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 approxi- mately 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](#_bookmark36),[20](#_bookmark48)].

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 (20e40 ◦C). Thermophilic

(45e65 ◦C) and extremophilic (≥75 ◦C) cultures have been also

studied [[21](#_bookmark49),[22](#_bookmark50)]. During DF, a mixture of volatile fatty acids (VFAs) and solvents esuch as acetic, lactic, butyric, propionic acids, and ethanol, among otherse is produced, its composi- tion 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](#_bookmark51),[24](#_bookmark52)]. 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](#_bookmark48),[25](#_bookmark53)e[27](#_bookmark53)]. 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 pro- duction *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](#_bookmark7). Despite the growing publication of research articles and re- views on DF, detailed quantitative comparisons and discus- sions 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, sub- strate 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 pro- duction by DF to industrial-scale are proposed to be explored.

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 Munic- ipal wastes. The description of each category eand sub- categoriese is included in [Table 1](#_bookmark9).

### Pretreatment classification

The pretreatment methods used in the research articles included in the database were classified into four categories: physical pretreatment, chemical pretreatment, physicochem- ical pretreatment, and biological pretreatment. The description of each category is included in [Table 2](#_bookmark10). The combination of two or more pretreatment methods in separate steps was consid- ered as Sequential pretreatments. The combinations identified in those studies included in the database are defined as follows: physical/chemical, physical/physicochemical, phys- ical/biological, and physical/chemical/biological. Exam- ples of each are shown in [Table 2](#_bookmark10).

### Starter cultures

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

follows:

# 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](#_bookmark178)].

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



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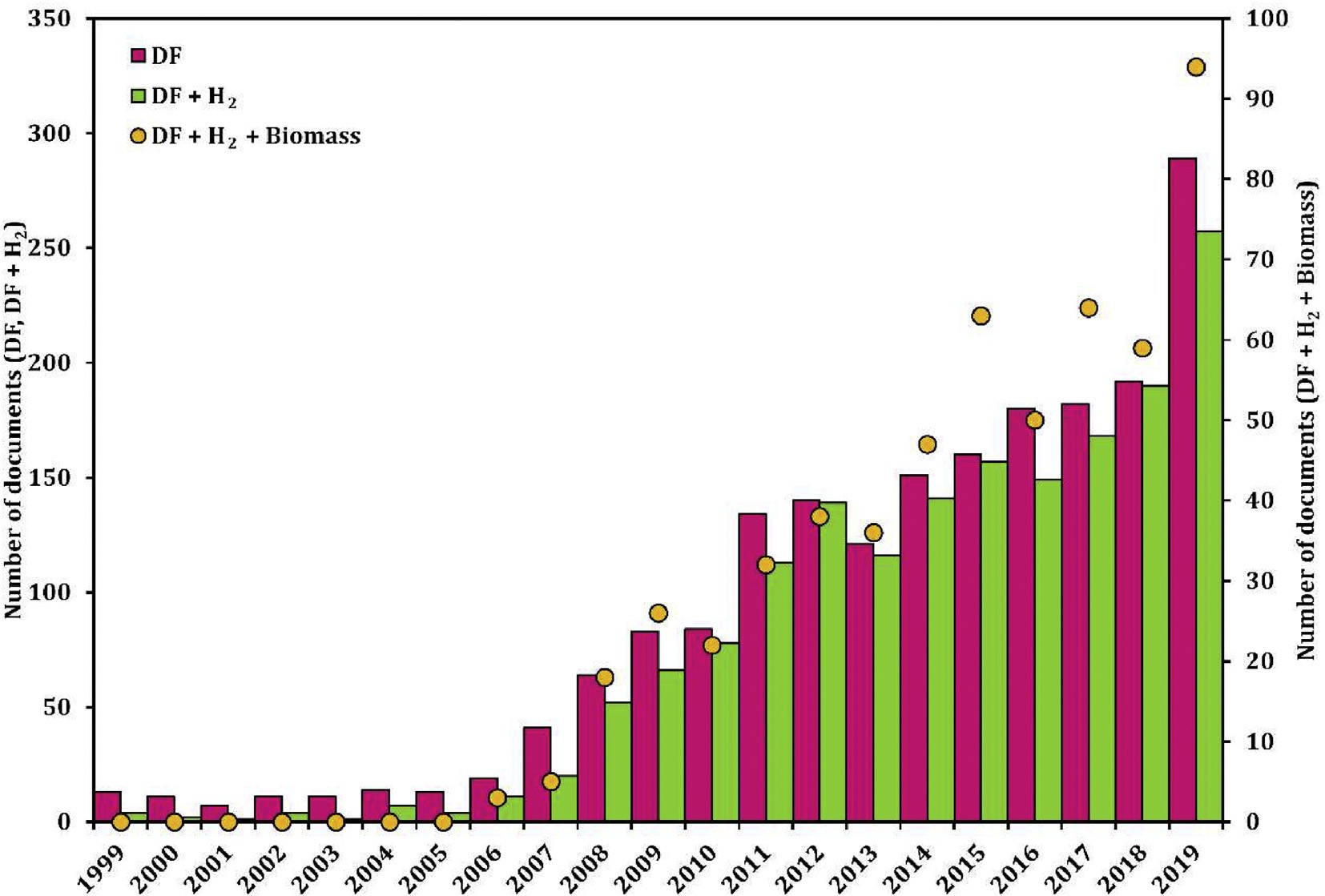


Fig. 1 e Publication of research studies related to hydrogen production from 1999 to 2019. DF, dark fermentation; H2, hydrogen production.

### Definition of response variables

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

* Hydrogen production (H2ac, 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 (*r*H2, mL H2/L∙h) is defined as the amount of hydrogen produced per unit of culture volume per unit of time.
* Hydrogen yield (*Y*H2, 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 produc- tion 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 (H2ac, *r*H2, *Y*H2) as a function of substrate concentration was divided into two main groups:

* G1, 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). G1 encloses 41 scientific articles.

* G2, encompassing studies reporting substrate concentra- tion as grams per litre of total solids (TS), volatile solids (VS), or volatile suspended solids (VSS). G2 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](#_bookmark55)e[31](#_bookmark55)]. The most popular similarity measures for continuous variables are the Euclidean dis- tance, the Mahalanobis distance and the Manhattan dis- tance. 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 concen-

tration, temperature, pH, H2ac, *r*H2, *Y*H2, 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](#_bookmark11). In matrix X1, the substrate concentration was reported as grams per litre of carbohydrate (monosaccharides and di- saccharides), total sugars, reducing sugars, COD, or TOC.



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Whereas in matrix X2, the substrate concentration was re- ported as grams per litre of TS, VS, or VSS. The analysis results were based on the Euclidean distance as a similarity measure

|  |  |  |  |
| --- | --- | --- | --- |
| Table 1 e Classification of feedstock used to produce hydrogen through dark fermentation. | | | |
| Category | Description | Subcategory | Biomass sourcea |
| Agricultural and green residues | Plant-derived biomass with a combined structure of cellulose, hemicellulose, and lignin [[251](#_bookmark247)]. 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](#_bookmark248)]), b) energy crops (crops cultivated specially to energy production [[253](#_bookmark249)]), c) green waste (conforming mainly by grass, leaves and fresh pruning originating from gardens and parks [[254](#_bookmark250)]; composting residues were also included as part of the green waste subcategory).  This category considers biomass produced by aquatic photosynthetic organisms [[255](#_bookmark251),[256](#_bookmark252)].  Feedstocks included in this category are products enot residues or wastese defined by the European Commission in its (EU) 2017/1017 Regulations provided in the European Union Catalogue of Feed Materials [[257](#_bookmark253)].  Liquid streams generated by industrial processes containing concentrations of hazardous and toxic substances affecting receiving waters and the aquatic ecosystem [[258e260](#_bookmark254)]. The effluents considered here are not from domestic sources.  The term municipal solid waste ewhich  consists primarily of wastepaper (~20%), green waste (~13%), food waste (~15%), and plastic (~13%)e is commonly used to group solid wastes generated by human settlements from household activities [[261](#_bookmark255) [e263](#_bookmark255)]. 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.  This waste is generated during the food supply chain (food production, processing, distribution, storage, sale, preparation, cooking, and serving) [[264](#_bookmark256)]. Several definitions of food waste can be found in the literature [[265](#_bookmark257),[266](#_bookmark258)]. In this work, food waste is defined according to the  FUSIONS0 Definitional Framework as any  food removed from the food supply chain  to be recovered or disposed of [[267](#_bookmark259)]. | Agriculture residues | 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, *Jatropha curcas* seed cake  Giant cane, sugar beet, *Paulownia*, energy poplar  Fallen leaves, compost waste  *Scenedesmus obliquus*, *Chlorella* sp., *Chlorella vulgaris*, *Spirogyra* sp., *Keratococcus*, *Oscillatoria Saccharina japonica*, *Laminaria japonica*, *Sargassum* sp.  *Pistia stratiotes*, *Eichhornia crassipes*, *Spartina anglica*  *Microcystis wesenbergii*, *Microcystis aeruginosaare*, *Arthrospira platensis* Cheese whey  Molasses  Wheat bran, malt powder, wheat starch  Vinasses (sugarcane, tequila, sugar beet)  Citrus fruit wastewater, nixtamalization wastewater, dairy wastewater  Palm oil mill effluent (POME), crude glycerol  Wastepaper towel  Solids residues from wastewater treatment  Vegetable peels, fruits peels, meat, fish, bread, rice, pasta  Waste from fruit processing factories (mainly fruit pulp), expired solid baby foods |
|  | Energy crops |
|  | Green waste. |
| Aquatic biomass | Microalgae |
|  | Seaweed |
|  | Aquatic weed |
|  | Cyanobacteria |
| Industrial derived products | Dairy products Agricultural products Cereal products |
| Industrial effluents | Sugar and ethanol industry effluents Industrial wastewater |
|  | Other industrial effluents |
| Municipal waste | Wastepaper Sewage sludge |
| Food waste | Domestic food waste |
|  | Food industry waste |
| a Based on information from the database. | | | |

and the Ward linkage algorithm which are common similarity

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

1

#

*ij*

*i*

*j*

"

*g*

*d* ¼ X *x* — *x g* ;

*k*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Table 2 e Classification of feedstock pretreatments using before hydrogen production through dark fermentation. | | | | |
| Pretreatment | Description | Examplesa | Reaction conditions | References |
| Physical | Modify particle size, surface area, crystallinity, | Chipping | Size reduction (10e25 mm of diameter) | [[270](#_bookmark262)] |
|  | and degree of polymerization of biomass without |  | Size reduction | [[51](#_bookmark73)] |
|  | using chemicals, enzymes, and microorganisms. | Aqueous extraction | 1:2 S/L, 25 ◦C, 6h | [[161](#_bookmark163)] |
|  | Physical pretreatment may enclose milling, |  |  |  |
|  | grinding, chipping, extrusion, ultrasonication, |  |  |  |
|  | electric field, and irradiation [[268](#_bookmark260),[269](#_bookmark261)]. |  |  |  |
| Chemical | Exert conformational changes in the biomass | Acid hydrolysis | 3% (v/v) H2SO4, 25 ◦C, 40 min | [[273](#_bookmark265)] |
|  | structure esuch as cleavage of bonds and | Acid-thermal | 2% (v/v) H2SO4, 140 ◦C, 4 bar, 0 h | [[274](#_bookmark266)] |
|  | generation of specific productse by the action of a | pretreatment | 4 M HCl, 120 ◦C, autoclave, 30 min | [[220](#_bookmark219)] |
|  | chemical reagent. The techniques of chemical |  |  |  |
|  | pretreatment comprise alkalis, acid, organosolv, |  |  |  |
|  | ionic liquids, and oxidative processes [[271](#_bookmark263),[272](#_bookmark264)]. |  |  |  |
|  | Variants in which high pressure and/or |  |  |  |
|  | temperature are used were also included in this |  |  |  |
|  | category. |  |  |  |
| Physicochemical | Combine physical changes and chemical | Hot-water hydrolysis | 100 ◦C, 1 h | [[277](#_bookmark269)] |
|  | reactions during processing. These | Hydrothermal | 80 ◦C, 1.5 h | [[278](#_bookmark270)] |
|  | pretreatments are performed at high | pretreatment | 121 ◦C, autoclave, 15 min | [[279](#_bookmark271)] |
|  | temperature and/or pressure with an inorganic | Steam explosion | Pre-soak: 1% (w/w) H2SO4, 30 ◦C, 30 min | [[280](#_bookmark272)] |
|  | compound which leads to disruption of biomass |  | 200 ◦C, 100 bars, 10 min |  |
|  | structure. Common physicochemical |  |  |  |
|  | pretreatments are steam explosion, ammonia |  |  |  |
|  | fibre explosion, carbon dioxide explosion, liquid |  |  |  |
|  | hot water, and hydrothermal liquefaction |  |  |  |
|  | [[275](#_bookmark267),[276](#_bookmark268)]. |  |  |  |
| Biological | Use of microorganisms (*i*.*e*., fungi, bacteria) or | Enzymatic hydrolysis | 80 U/g-biomass cellulose, 92 U/g-biomass a- | [[283](#_bookmark275)] |
|  | eeither crude, pure or partially purifiede |  | amylase, 120 U/g-biomass glucoamylase, 50 ◦C, |  |
|  | enzymes (*e*.*g*., laccases, peroxidases, cellulases, |  | 12 h |  |
|  | hemicellulases) for the selective degradation of | Microbial-enzymatic | *Bacillus* sp., *B. sphaericus*, *B. subtilis*, *B. thuringiensis*, | [[284](#_bookmark276)] |
|  | biomass components [[281](#_bookmark273),[282](#_bookmark274)]. | hydrolysis | *Proteus mirabilis* strains (37 ◦C, 2 d) |  |
| Sequential pretreatment |  |  |  |  |
| Physical/Chemical | Involves the use of a physical pretreatment | Milling / Alkaline | Size reduction (0.75 mm) | [[285](#_bookmark277)] |
|  | method followed by a chemical pretreatment | hydrolysis | 21% (v/v) MEA, 65 ◦C, 16 h |  |
|  | method (*e.g.*, milling followed by acid/base | Chopped / Acid | Size reduction (2e3 mm) | [[286](#_bookmark278)] |
| Physical/Physicochemical | hydrolysis).  Is a combination of a physical pretreatment | hydrolysis  Comminuted / | 2% (v/v) H2SO4, 121 ◦C, 15 lbs, 90 min Size reduction (<0.88 mm) | [[287](#_bookmark279)] |
|  | method followed by another physicochemical | Microwave-acid | 1% (v/v) H2SO4, 2450 MHz, 140 ◦C, 15 min |  |
|  | (*e.g.*, milling followed by steam explosion). | pretreatment |  |  |
|  |  | Milling / Steam | Size reduction (<0.5 cm) | [[288](#_bookmark280)] |
|  |  | explosion | 198 ◦C, 1.5 Mpa, 1.5 min |  |



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Physical/Biological

Refers to a combination of a physical pretreatment method followed by a biological pretreatment method (*e.g.*, griding followed by enzymatic hydrolysis).

Physical/Chemical/Biological

Considers the combination of a physical pretreatment method with a chemical pretreatment method, to later apply a biological pretreatment method (*e.g.*, milling followed by acid/base hydrolysis and followed by enzymatic hydrolysis).

a Based on examples from the database.



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where *g* denotes the number of the variables (parameters). If *g* is equal to 2, *dij* is represented by the Euclidean distance. If *g* is equal to 1, *dij* represents the Manhattan distance. A colourmap was constructed as an interpretation of objects in the pa- rameters space and parameters in the object space [[32](#_bookmark56)e[34](#_bookmark56)]. In the colourmap, all measured parameters are presented in the form of colour images with pixels representing the data ma- trix elements and sorted according to the order given. With the simultaneous interpretation of dendrograms and the col- ourmap, relationships between operational conditions (*e.g.*, temperature, pH, working volume, substrate concentration) and response variables (*e.g.*, yields, productivity) were identified.

Size reduction (40-mesh)

1% (w/w) biomass, 1% (w/w) cellulase, pH 4.8,

50 ◦C, 150 rpm, 48 h

Size reduction (<40-mesh)

Pretreated with *Phanerochaete chrysosporium*

(29 ◦C, 21 d, 70% moisture)

Enzymatic hydrolysis with *Trichoderma viride* [3.5% (w/v) biomass, pH 5.0, 50 ◦C, 130 rpm, 96 h] 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 Size reduction (1e2 mm)

6% (v/v) H2SO4, 120 ◦C, 0.9 MPa, 60 min

1.17 mg cellulase/mL, 45 ◦C, pH 5.0

[289]

[162]

[219]

[160]

# 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](#_bookmark57)]. Metabolic diversity en- ables microorganisms to use different biomasses as a sub- strate. The process to produce H2 *via* DF using the biomass is sketched in [Fig. 2](#_bookmark12)A. A thermochemical pretreatment may be required before DF to make biomass sugars available to DF.

Grinding / Enzymatic hydrolysis

Grinding / [Microbial-](#_bookmark57) enzymatic hydrolysis

Milling / Alkaline hydrolysis / Enzymatic hydrolysis

Milling / Acid hydrolysis / Enzymatic hydrolysis

|  |  |  |  |
| --- | --- | --- | --- |
| Table 3 e Studied parameters in the chemometric analysis. | | | |
| A. Parameters considered in Matrix X1  No. Parameter Symbol | | | Unit |
| 1  2 | Substrate concentrationa Temperature | *S*  T | g/L  oC |
| 3 | pH | pH | e |
| 4  5 | Working volume  Hydrogen production rate | Vw  *r*H2 | L  mL H2/L∙h |
| 6 | Hydrogen yield | *Y*H2 | mL H2/g substratea |
| 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 | EtCO2 | g/L |
| B. Parameters considered in Matrix X2  No. Parameter Symbol | | | Unit |
| 1  2 | Substrate concentrationb Temperature | *S*  T | g/L  oC |
| 3 | pH | pH | e |
| 4 | Working volume | Vw | L |
| 5  6 | Hydrogen production  Hydrogen production rate | H2ac  *r*H2 | mL H2/L  mL H2/L∙h |
| 7 | Hydrogen yield | *Y*H2 | mL H2/g substrateb |
| 8 | Acetate | AcOH | g/L |
| 9 | Butyrate | BTA | g/L |
| 10 | Ethanol | EtOH | g/L |
| 11 | Propionate | EtCO2 | g/L |
| a Substrate concentration reported as grams per litre of carbohy- drate (monosaccharides and disaccharides), total sugars, reducing sugars, chemical oxygen demand, or total organic car- bon;b Substrate concentration reported as grams per litre of total solids, volatile solids total volatile solids or volatile suspended solids. | | | |



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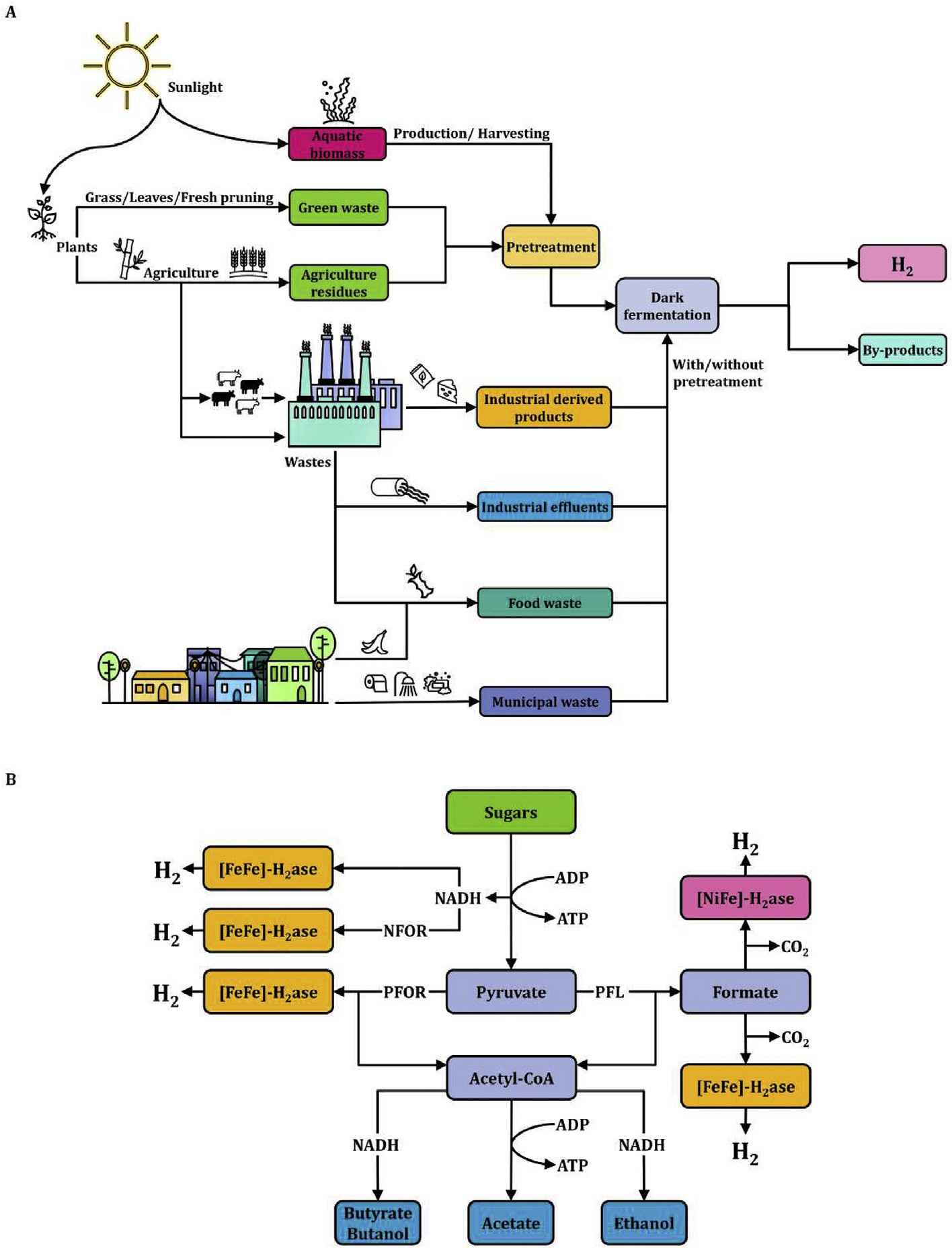


Fig. 2 e Production of hydrogen *via* dark fermentation from biomass. Biomass converted into H2, a general description (A). Typical metabolic pathways leading to H2 production in dark fermentation [[4](#_bookmark36),[21](#_bookmark49)] (B). NADH, nicotinamide adenine dinucleotide; NFOR, nicotinamide adenine dinucleotide hydrogen (reduced) ferredoxin oxidoreductase; PFOR, pyruvate ferredoxin oxidoreductase; PFL, pyruvate formate lyase.

Feedstocks employed in DF are composed of several compo- nents (*e.g.*, carbohydrates, proteins, lipids), as described in Section [Feedstocks for hydrogen production](#_bookmark15). Carbohydrates can be hydrolysed into simple sugars, which are metabolized by certain bacteria to H2 production. During DF, these sugars are converted into pyruvate *via* glycolysis ([Fig. 2](#_bookmark12)B), 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, CO2, and reduced ferredoxin. The latter is involved in the reduction of [FeFe]-hydrogenases, which subsequently reduce protons yielding H2. If PFL is

used, the products are acetyl-CoA and formate. The latter is converted to H2 and CO2 in the presence of [FeFe]- hydrogenases or [NiFe]-hydrogenases [[4](#_bookmark36)]. 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](#_bookmark58)]: (i) Sticklan reaction, (ii) oxidative deamination from a sole AA, (iii) reductive deamination from a sole AA ([Table 4](#_bookmark13)). Approxi- mately 90% of AA degradation is controlled by the first reac- tion but it does not imply H2 production. The second one, involving H2 production, is thermodynamically unfavourable



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unless H2 partial pressure is maintained to an extremely low

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| Table 4 e Reactions involves in fermentation of proteins and lipids under anaerobic conditions. |
| Protein degradation |
| Sticklan reaction  Alanine þ 2Glycine / 3Acetate þ 3NH3 þ  CO2  Oxidative deamination from a sole AA D*G*0 ¼þ 4.2 kJ/mol Leucine þ 3H2O / Isovalerate þ  HCO—3 NHþ4 þ 2H2  Reductive deamination from a sole AA D*G*0 ¼ e 77.8 kJ/mol Glycine þ H2 / Acetate þ NH3  Lipid degradation  0  *n*-LCFA / (*n*e*2*) eLCFA þ 2Acetate þ 2H2 D*G* ¼þ 48 kJ/mol  0  Pyruvate þ Acetate þ 2H2 / CO2 þ 3H2O D*G* ¼ e 95.4 kJ/mol |
| LCFA: long chain fatty acids. |

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 in- volves H2-consuming reactions [[37](#_bookmark59)]. 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](#_bookmark13)) under very low H2 partial pressure (below 10—3 atm) [[36](#_bookmark58)]. Moreover, LCFA may inhibit anaerobic bacteria. They adhere to the cell wall restricting nutrient transportation [[37](#_bookmark59)]. Since higher *Y*H2 can be obtained with carbohydrates-rich feedstocks than with

protein- and lipid-rich feedstock [[38](#_bookmark60)], the selection and eval- uation of feedstocks for H2 production is a crucial step for developing robust DF processes.

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| Table 5 e Description of feedstocks used for H2 production *via* dark fermentation. | | |
| Feedstock | Characteristics | References |
| Agricultural and green residues  Aquatic biomass  Industrial derived Dairy products products  Agricultural products  Cereal products  Industrial effluents Sugar and ethanol industry effluents Industrial wastewaters  Other industrial effluents  Municipal wastes Wastepaper  Sewage sludge  Food waste | Available in large quantities (10e50 billion tonnes per year), low price, and renewable.  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.  Not part of the human food supply chain.  Cheese whey. Worldwide estimated production of 108e1.9 × 108 tonnes per year (10 L cheese whey/kg cheese). High lactose content, as well as nutrients for microbial growth.  Molasses. Available (~50 million tonnes worldwide production per year) and low cost, contain high amounts of sugar.  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.  Vinasses are acidic suspensions of organic matter with high COD values, rich in phenolic compounds and melanoidins, containing minerals and small quantities of nonfermented sugar.  Nixtamalization wastewaters (~12e14 million m3 of wastewater per year,  Mexico) contains high organic matter (COD and BOD), as well as carbohydrates, calcium, phenolic compounds, and proteins.  Citrus wastewaters (1e17 m3 per ton of citrus fruit processed) are rich in  organic matter and nutrients, besides heaving a low pH and high corrosivity, could hold essential oils in trace.  Dairy wastewater (~6e10 L wastewater/L processed milk) have suspended  solids, organic matter, high content of nitrogen and phosphorous, as well as oil and greases.  Crude glycerol (0.1 kg glycerol/kg biodiesel produced) is an inexpensive carbon source for microorganisms growing and microbial products.  Palm oil mill effluent (3.05 ton/ton of crude palm oil produced) is rich in carbohydrates, proteins, nitrogenous compounds, minerals, and lipids. 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).  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.  Abundant (1.3 billion tonnes food per year) carbon source. May comprise a  mixture of carbohydrates, lipids, and proteins. | [[99](#_bookmark109),[290](#_bookmark282),[291](#_bookmark283)]  [[282](#_bookmark274),[292](#_bookmark284)]  [[293](#_bookmark285),[294](#_bookmark286)]  [[295e297](#_bookmark287)] [[298](#_bookmark288),[299](#_bookmark289)]  [[300](#_bookmark290),[301](#_bookmark291)]  [[302](#_bookmark292),[303](#_bookmark293)] [[304e307](#_bookmark294)]  [[308e311](#_bookmark295)]  [[312e314](#_bookmark296)]  [[3](#_bookmark35),[315](#_bookmark297),[316](#_bookmark298)]  [[317e319](#_bookmark299)] [[320e323](#_bookmark300)] [[261](#_bookmark255),[324e326](#_bookmark301)]  [[327](#_bookmark302),[328](#_bookmark303)]  [[329e331](#_bookmark304)] |



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

*Feedstocks for hydrogen production*

As described in Section [Feedstock classification](#_bookmark2), the feed- stocks were classified into six categories. [Table 5](#_bookmark14) includes a description of the feedstock categories considered in this work together with their associated references. The Agricul- tural and green residues, the most abundant renewable ma- terial on earth [[39](#_bookmark61),[40](#_bookmark62)] was employed in 36.5% of the articles included in the database, as shown in [Fig. 3](#_bookmark16). 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](#_bookmark17). 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 hemi- celluloses and to release cellulose for the enzymatic hydro- lysis [[35](#_bookmark57),[41](#_bookmark63)].

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](#_bookmark18)). The lignin mass percentage (≤20% w/w) is usually

lower than many agricultural and green residues, making its saccharification easier than of lignocellulosic biomass [[42](#_bookmark64),[43](#_bookmark65)]. 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](#_bookmark66)e[48](#_bookmark66)].

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 enot residues or wastese whose composition depends on their

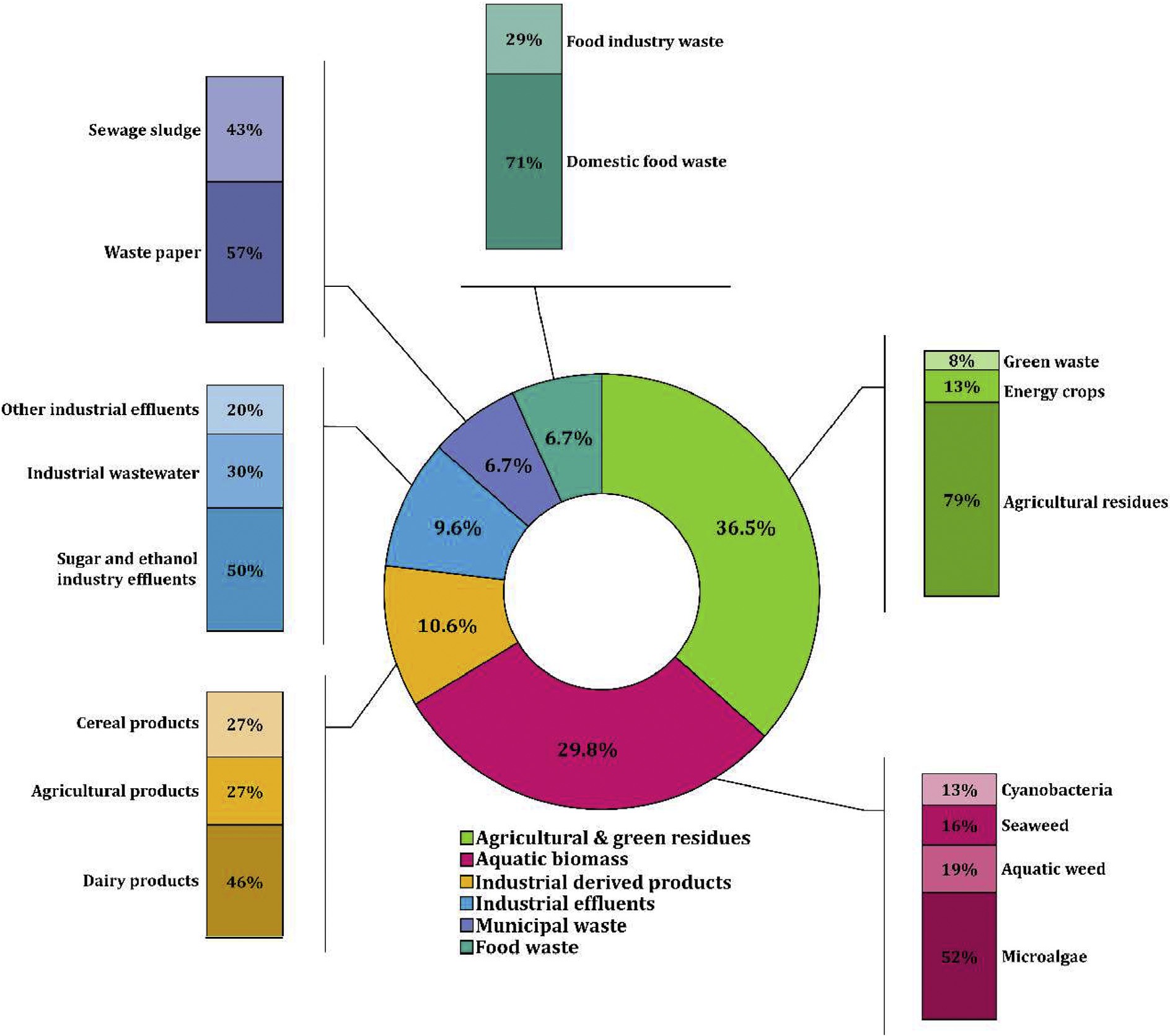


Fig. 3 e Feedstock commonly used to produce hydrogen with dark fermentation.



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| Table 6 e Composition (*wt%*) of agricultural and green residues. |
| Category Subcategory Biomass Solids and moisture Protein Lipid Extractives Structural Total Carb. TOC Elemental C/N Reference  composition analysis    TS VS Ash Moist. Cell. Hemic. Lignin C H O N S |
| Agricultural Agricultural Energetic willow wood 8.5 46.5 15.6 29.4 [[285](#_bookmark277)]  & green residues residues Pine tree wood pellet 1.3 0.1 39.5 22.1 37.1 [[332](#_bookmark305)]  Paulownia 4.3 13.0 34.6 19.3 15.9 [[289](#_bookmark281)]  Cornstalk 84.6 [[219](#_bookmark218)]  Rice straw 32.1 30.3 17.0 [[286](#_bookmark278)]  Rice husk 16.0 5.7 40.3 12.5 25.4 [[163](#_bookmark165)]  Rice straw 92.3 80.9 [[333](#_bookmark306)]  Wheat straw 44.5 19.2 5.8 [[334](#_bookmark307)]  93.5 89.4 [[335](#_bookmark308)]  Sugarcane top 7.5 39.0 20.0 21.5 [[210](#_bookmark210)]  Agave bagasse 17.5 56.4 10.9 15.2 [[336](#_bookmark309)]  Cashew apple bagasse 65.7 1.1 8.4 20.6 10.2 35.3 50.5 5.7 1.4 [[337](#_bookmark310)]  Sugarcane bagasse 91.8 1.9 8.2 [[338](#_bookmark311)]  97.2 42.3 21.0 18.4 45.2 6.8 1.7 0.2 26.0 [[211](#_bookmark211)]  Empty fruit bunch of 39.8 1.4 38.3 11.1 9.4 [[160](#_bookmark162)] oil palm  Cassava residues 5.5 47.6 16.3 19.5 [[270](#_bookmark262)]  Carob pulp 3.5 5.4 0.6 32.9 46.6 [[161](#_bookmark163)]  Sunflower stalks 96.4a 89.4a 25.1b 11.6b 32.5b [[339](#_bookmark312)]  *Jatropha curcas* seed cake 867.8c 13.7 [[116](#_bookmark126)]  Energy crops Energy poplar 0.1 3.5 6.4e8.4 39.5 22.2 26.3 [[340](#_bookmark313)]  Giant cane 36.1d 21.0d 24.3d [[243](#_bookmark239)] Green waste Fallen leaves 91.6 80.4 101.7e 414.2e 46.8 6.1 1.4 33.2 [[341](#_bookmark314)]  91.5 32.5 19.7 30.1 [[209](#_bookmark209)]  Green waste (compost waste) 657c 24.0 39.0 200.0 [[342](#_bookmark315)] |
| TS: Total solids; VS: Volatile solids; TOC: Total organic carbon; C/N: carbon-nitrogen ratio.  awet weight %;b VS%;c g/kg substrate;d TS%;e mg/g-TS. |



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| Table 7 e Composition (*wt%*) of aquatic biomass. |
| Category Subcategory Biomass Solids and Protein Lipid FAME Structural Total COD Elemental C/N Minerals Reference moisture composition Carb. analysis    TS VS SS DS Ash Moist. Cell. Hemic. Lignin C H O N S |
| Aquatic Microalgae *Scenedesmus* 20.2 22.6 55.4 44.3 7.8 44.3 3.2 0.4 13.7 [[44](#_bookmark66)]  biomass *obliquus* 92.4 88.4 0.3a 1.4a [[45](#_bookmark67)]  75.5 5.4 20.4 17.1 30.7 20.2 [[343](#_bookmark316),[344](#_bookmark317)]  35.7 25.2 42.6 [[279](#_bookmark271)]  31.4 17.9 4.4 30.2 [[345](#_bookmark318)]  *Chlorella* sp. 97.5 92.5 5.1 4.7 52.3 8.7 29.2 47.2 6.5 30.2 8.4 0.6 5.6 [[283](#_bookmark275)]  *Chlorella vulgaris* 45.6 [[346](#_bookmark319)]  *Spirogyra* sp. 5.4 23.2 14.2 27.0 [[347](#_bookmark320)]  Consortia 50.0 19.0 20.0 [[214](#_bookmark213)] (*Scenedesmus*,  *Keratococcus*, *Oscillatoria)*  Undefined 12.2b 6.3b 43c [[348](#_bookmark321)] consortia  Seaweed *Saccharina* 82.8d 80 998e 40.1f 5.5f 45.6f 2.5f [[46](#_bookmark68)]  *japonica*  *Laminaria japonica* 98.3 82.8d 17.2d 15.6f 0.8f 998e 40.1f 5.5f 45.6f 2.5f 16.0 [[287](#_bookmark279)]  *Sargassum* sp. 896g 490g 13g 32.9f 11.7f 3.3f 600g [[215](#_bookmark214)] Aquatic weed *Pistia stratiotes* 36.0 23.0 3.0 [[48](#_bookmark70)]  37.8 25.3 [[273](#_bookmark265)]  *Eichhornia* 89.1 42.9 57.1 10.9 9.8 24.8 30.0 5.6 1.8h 31.5 6.2 31.7 2.8 11.0 [[115](#_bookmark125)]  *crassipes* 22.3 39.8 20.6 [[349](#_bookmark322)]  *Spartina anglica* 97.2 86.3 10.9 2.8 38.7f 19.2f 8.9f 39.2d 5.0d 38.2d 1.2d 0.5d [[139](#_bookmark144)]  Cyanobacteria *Microcystis* 53.7 32.7 13.8 36.6 3.1 11.6 20.9 3.7 25.0 3.1 0.8 [[212](#_bookmark212)]  *wesenbergii*, 55.0 36.6 38.3 2.5 15.1 24.1 4.9 25.3 2.6 0.8 [[135](#_bookmark141)]  *Microcystis aeruginosaare*  *Arthrospira* 13.0 53.4 [[138](#_bookmark145)]  *platensis* |
| 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/L;d TS%;e mg/g-TS;f VS%;g mg/g substrate;h g/g substrate. |



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origin, as shown in [Table 8](#_bookmark21)), Industrial effluents (composed mainly of degradable organic matter which can be converted into H2 by DF [[49](#_bookmark71)], see [Table 8](#_bookmark21)), Municipal (wastepaper and sewage sludge, see [Table 9](#_bookmark23)) and Food waste (see [Table 9](#_bookmark23) for composition details), respectively.

### Feedstock pretreatment methods

Despite their complex structure, some feedstock can be con- verted directly into H2 without pretreatment. According to the database of this work, 28% of the studies used unpretreated feedstocks to perform DF ([Fig. 4](#_bookmark24)A). The most employed feed- stocks without pretreatment fall in Industrial-derived prod- ucts and Industrial effluents categories. These feedstocks contain carbohydrates (*e*.*g*., lactose, sucrose, total carbohy- drates, 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](#_bookmark72)e[54](#_bookmark72)]. 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 con- version, feedstocks must be pretreated. Feedstocks in Agri- cultural and green residues and Aquatic biomass categories were usually pretreated, as shown in [Fig. 4](#_bookmark24)A.

Pretreatments before DF can be employed alone or com- bined, as shown in [Fig. 4](#_bookmark24)B. 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 re- quirements and environmental impacts capital (CAPEX) and operational (OPEX) costs [[55](#_bookmark74),[56](#_bookmark75)].

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. 4](#_bookmark24)B). Regarding single pretreatments, acid hydrolysis ein all its variants (*i*.*e*., room temperature, high temperature/pressure)e was the only chemical pretreatment employed alone. Other single pre- treatments were heat pretreatment (*i*.*e*., high temperature, autoclavation 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 pre- treatments (see Section [Pretreatment classification](#_bookmark3)), the combination of physical with chemical methods was the most employed (53%), as shown in [Fig. 4](#_bookmark24)B. 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 phys- ical/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 pre- treatments (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 microorgan- isms that can degrade and convert biomass into H2 and other by-products. The bacteria —22 different genuse reported for

H2 production in the research studies considered in the

database are shown in [Fig. 5](#_bookmark25).

*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](#_bookmark76)]. However, *Clostridium* species such as *C. butyricum*, *C. acetobu- tylicum*, *C. beijirinkii*, *C. pasteurianum*, and *C. tyrobutyricum* can utilize the PFL system [[58](#_bookmark77)]. In facultative bacteria esuch as *Enterobacter* and *Escherichia*e H2 can be produced from formate *via* the PFL system by the action of [NiFe]-hydrogenases [[59](#_bookmark78),[60](#_bookmark79)]. *Bacillus* isolates are capable to produce hydrogen using biomass esuch as palm oil mill effluent (POME), food wastes, molasses and ethanol refinery wastewatere as sub- strate [[61](#_bookmark80)e[64](#_bookmark80)]. Also, some species of *Bacillus* such as *B. coagu- lans* can convert pyruvate to acetyl-CoA *via* the PFL system [[65](#_bookmark81)]. However, the effects on DF using mixed cultures *Bacillus* may be either positive (*e*.*g*., creating an anaerobic environ- ment) or negative (*e*.*g*., increasing lactate concentration and decreasing H2 production), which depends on operational conditions such as substrate concentration and temperature [[66](#_bookmark82)]. The presence of *Streptococcus* is mainly associated with auto aggregation of biomass by the accumulation of extra- cellular substances which maintain the structure of granules preventing their disintegration [[67](#_bookmark83)]. *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](#_bookmark84)e[71](#_bookmark84)].

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 microor- ganisms were not found in the literature with the keywords mentioned in Section [Database](#_bookmark4). While mixed cultures were reported using all feedstock categories, pure cultures were only reported in studies that employed biomass as the sub- strate of Agricultural and green residues, Aquatic biomass, and Industrial-derived products categories ([Table 10](#_bookmark26)).

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



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| Table 8 e Composition (*wt%*) of industrial derived products and industrial effluents. | | | | | | | | | | | | | | | | | | |
| Category | Subcategory | Biomass | TS | VS | Solids SS | and moisture VSS DS | | Ash | Moist. | Protein | Lipid | Extractives | Cellulose | Total Carb. | TRS | Carbohydrates Lactose Sucrose | | Fructose |
| Industrial | Dairy | Cheese whey |  |  |  |  |  |  |  |  |  |  |  |  |  | 75.5 |  |  |
| derived | products | powder |  |  |  |  |  |  |  | 13.3 | 1 |  |  | 76.5 |  |  |  |  |
| products |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.0 |  |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 75.5 |  |  |
|  |  |  | 166a | 152a |  |  |  |  |  |  |  |  |  |  |  | 154a |  |  |
|  | Agricultural | Molasses |  |  |  |  |  | 4e8 |  |  |  |  |  | 48e58 |  |  |  |  |
|  | products |  |  |  | 140a | 121a |  |  |  | 0.7a |  |  |  |  |  |  | 760a | 6.2a |
|  | Cereal | Wheat bran | 92.5 | 95.4b |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | products | Malt powder |  |  |  |  |  |  |  | 6.2 |  |  | 68 |  |  |  |  |  |
| Industrial | Sugar and | Tequila | 34.5 | 30.9 |  |  |  |  |  | 0.1 |  | 0.5 |  | 14.5 | 8.2 |  |  |  |
| effluents | ethanol | vinassea | 43.8 | 37.4 |  |  | 28.8 |  |  |  |  | 1.5 |  | 19.6 | 11.0 |  |  |  |
|  | industry | Sugarcane |  |  |  | 5.5 |  |  |  |  |  |  |  | 5.0 |  |  |  |  |
|  | effluents | vinassea |  |  |  | 5.5 |  |  |  |  |  |  |  | 5.5 |  |  |  |  |
|  | Industrial | Nixtamalization | 24.5 | 19.3 |  |  |  |  |  | 1.3 |  | 0.6 |  | 16.0 | 0.2 |  |  |  |
|  | wastewater | wastewatera |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Citrus processing |  |  | 0.6 |  |  |  |  |  |  |  |  |  |  |  |  | 3.9 |
|  |  | industry wastewater |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Dairy wastewater | 10.4 |  | 1.6 |  |  | 8.8 |  |  |  |  |  |  |  |  |  |  |
|  | Other | Crude glycerol |  |  |  |  |  | 4.8 | 40.5 |  |  |  |  |  |  |  |  |  |
|  | industrial | Palm oil mill effluent |  |  | 18.8 |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | effluents |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 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](#_bookmark85),[73](#_bookmark86)]. In undefined mixed cultures, the microbial diversity is usually dominated by *Clostridium* strains. Only few studies reported the dominance of *Enterobacter*, *Ruminococcus*, *Bacillus* or *Pecti- natus* 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](#_bookmark87),[75](#_bookmark88)]. *Pectinatus* are butyrate-type fermenta- tive bacteria, capable to adapt to brewery environments, producing mainly H2, acetic and butyric acids from carbohy- drates [[76](#_bookmark89)e[78](#_bookmark89)]. In 46% of undefined mixed cultures, *Clostridium* and *Enterobacter* strains appear together. The interaction be- tween *Clostridium* and *Enterobacter* is beneficial to H2 produc- tion since *Enterobacter* can remove oxygen and generate anaerobic conditions needed by strict anaerobes, such as *Clostridium* [[66](#_bookmark82),[79](#_bookmark91),[80](#_bookmark92)]. Although *Clostridium*/*Enterobacter* in- teractions are beneficial for H2 production, other concomitant bacteria may accompany mixed cultures. Hydrogenic bacteria (*e*.*g*., *Lachnxospira*, *Citrobacter*, *Enterococcus*, *Paraclostridium*), as well as bacteria with hydrolytic abilities or capacity to main- tain an anaerobic environment (*e*.*g*., *Klebsiella*, *Burkholderia*, *Pseudomonas*), may be beneficial for H2 performance. However, no-hydrogenic or hydrogen consumed or substrate compet- itor (*e*.*g*., *Terrisporobacter*, *Streptococcus*, *Lactobacillus*) bacteria

Defined mixed cultures e*i.e.,* synthetic/artificial microbial consortia or co-culturee involve the employment of comple- mentary 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 opera- tional stability and substrate consumption, as well as the in- crease of production yields [[73](#_bookmark86),[86](#_bookmark96),[87](#_bookmark97)]. Defined mixed cultures reported in the studies included in the database were *C*. *pas- teurianum*/*B*. *subtilis*, C. cellulolyticum/C. amalonaticus, *E. coli*/

C. acetobutylicum, *B. cereus*/*B. pumilus*/*Bacillus* sp./*B. thur- ingiensis*/*E. aerogenes*/*P. mirabilis*, and *E. coli*/*E. cloacae*, using sugarcane bagasse hydrolysate, pretreated corn stover, cya- nobacteria hydrolysate, food waste hydrolysate, and crude glycerol as substrate, respectively.

Among all microbial genera reported, only *Clostridium*, *Enterobacter*, *Bacillus*w *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 *Caldi- cellulosiruptor saccharolyticus* were employed in fermentations with feedstocks of the Aquatic biomass category. And *C*. *ace- tobutylicum* was used to obtain H2 from molasses belonging to the Industrial-derived products category.

can also be found in mixed cultures [[66](#_bookmark82),[81](#_bookmark93)e[84](#_bookmark93)]. Their abun-

dance is determined by operation parameters (*e.g.*, pH, tem- perature, feedstock), source and pretreatment of inoculum, and process enhancement methods (*e.g.*, additives, co- digestion, substrate pretreatment) [[85](#_bookmark95)].

# Production performance

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



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|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Carbohydrates Organic matter N C/N Glycerol Acetate Propionate Lactate Butyrate i-Butyrate Ethanol Methanol Na Minerals Reference Glucose Starch COD BOD TOC | | | | | | | | | | | | | | | | | |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | [[350](#_bookmark323)] |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 1.1 | 7.6 | [[150](#_bookmark154)] |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | [[334](#_bookmark307)] |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | [[58](#_bookmark77)] |
|  |  | 176a |  |  |  |  |  |  |  | 3.1a |  |  |  |  | 3.2a |  | [[136](#_bookmark142)] |
|  |  |  |  | 28e34 | 0.2e2.8 |  |  |  |  |  |  |  |  |  |  |  | [[236](#_bookmark232)] |
|  |  | 1331a |  |  | 16a |  |  | 17.7a | 28.7a | 51.1a | 2.5a | 2.2a |  |  |  |  | [[351](#_bookmark324)] |
|  | 5.8b |  |  |  | 2.6b | 16.9 |  |  |  |  |  |  |  |  |  |  | [[165](#_bookmark167)] |
|  | 63.7 |  |  | 85.2 |  |  |  |  |  |  |  |  |  |  |  |  | [[352](#_bookmark325)] |
|  |  | 59.7 | 30.6 | 15.8 | 0.2 |  |  |  |  |  |  |  |  |  |  |  | [[109](#_bookmark118)] |
|  |  | 63.1 | 29.2 |  | 0.2 |  |  |  |  |  |  |  |  |  |  |  | [[164](#_bookmark166)] |
|  |  | 49.0 | 23.2 |  |  |  | 3.3 | 1.1 | 0.1 | 1.7 | 0.5 |  | 5.5 | 0.4 |  |  | [[110](#_bookmark120)] |
|  |  | 32.3 | 15.4 |  |  |  |  | 3.0 |  | 1.8 |  |  |  |  |  |  | [[111](#_bookmark121)] |
|  |  | 25.1 | 14.0 | 8.7 | 0.4 |  |  |  |  |  |  |  |  |  |  |  | [[109](#_bookmark118)] |
| 12.5 |  | 19.5 |  |  |  |  |  |  |  |  |  |  |  |  |  |  | [[112](#_bookmark122)] |
|  |  | 11 | 7.2 |  |  |  |  |  |  |  |  |  |  |  |  |  | [[353](#_bookmark326)] |
|  |  |  |  |  |  |  | 47.5 |  |  |  |  |  |  |  |  |  | [[113](#_bookmark123)] |
|  |  | 49.8 | 22.5 |  | 4.3 |  |  |  |  |  |  |  |  |  |  |  | [[354](#_bookmark327)] |

H2 production performance, considering operational condi- tions (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. 6](#_bookmark27)A

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 *Y*H2 obtained at thermophilic conditions [[88](#_bookmark98),[89](#_bookmark99)]. 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

1e2 fold more H2 than a mesophilic community dominated by *Clostridium* [[90](#_bookmark100)]. However, DF must operate at near-ambient temperatures to obtain a positive net energy gain[3](#_bookmark22) [[91](#_bookmark101)].

pH may affect substrate hydrolysis, hydrogenase activity and the metabolic pathways, as well as microbial community structure during DF [[92](#_bookmark102)]. [Fig. 6](#_bookmark27)B 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) 4e4.25 in 2% of the studies, b) 5e6.5 in 52% of the scientific articles, c) > 6.5e8 in 43% of the studies, and d) >8e10 in 3% of the studies. Although hydrogenic pathways are usually established at pH values approximately 4.5e6.5, initial pH may influence H2 production [[93](#_bookmark103)]. For example, in studies using different substrates (duckweed [[94](#_bookmark104)], kitchen waste [[95](#_bookmark105)], liquid scotta permeate [[96](#_bookmark106)], cattle slaughterhouse wastewater [[97](#_bookmark107)]), the initial pH, which improves H2 production, was reported in the range of 7e8.5.

3 Defined as the total energy produced equivalent to the H2 volume generated by DF minus any heat energy required to raise the reactor contents from ambient temperature to the fermen- tation temperature.

T and pH play an important role in DF because H2 pro- duction can be inhibited if these variables do not have appropriate values [[98](#_bookmark108)]. Furthermore, optimal conditions of T and pH may depend on the type of substrate and source of inoculum used [[99](#_bookmark109)].

Conversion of biomass into H2 can contribute towards future energy needs. However, studies at pilot and large scales must be carried out to prove the profitability of H2 production *via* DF [[100](#_bookmark110)]. According to the database, the average working volume (Vw) employed was 0.6 ± 1 L. All feedstocks were mainly fermented in Vw between 0.016 and 1.2 L, as shown in [Fig. 6](#_bookmark27)C. Few studies were found with Vw between 1.5 and 4.5. Only one work reported a Vw 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 eval- uate kinetic and stoichiometric parameters, different sub- strates, as well as to perform inhibition assays [[67](#_bookmark83)]. 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 opera- tion, 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](#_bookmark111)]. 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](#_bookmark83),[101](#_bookmark111)]. SBR and GSBR were employed in 21.4% and 4.2% of the works, respectively. The advantages of SBR are diverse control stra- tegies, decoupling solid and hydraulic retention times, usage of a large variety of instrumentation, flexible operation, and low cost. Their disadvantages are related to microbial



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community structure (methanogenic archaea, homoaceto- genic bacteria, and propionic and lactic acid bacteria) [[101](#_bookmark111),[102](#_bookmark112)]. GSBR is characterized by biomass retentions through the formation of self-aggregated granules. Never- theless, the formation of these granules depends on the presence of exopolysaccharide forming microbes [[101](#_bookmark111),[103](#_bookmark113)].

Elemental C/N Reference analysis

S

[355]

[203]

[341]

[356]

[357]

[358]

[356]

[359]

[173]

[360]

[277]

5.4

11.0

TS: Total solids; VS: Volatile solids; SS: Suspended solids; VSS: Volatile 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.

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

As explained in Section [Data organization](#_bookmark8), the data was organized into two groups, G1 and G2, to facilitate its analysis. In G1, most studies employed substrate concentrations (*S*) ranging 0.6e36.9 g/L. Few studies were found with *S* surpass- ing 46 g/L. The average was 16.1 ± 14.4 g/L, as shown in [Fig. 7](#_bookmark28)A. 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. 7](#_bookmark28)B. Concerning *r*H2, [Fig. 7](#_bookmark28)C 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 *Y*H2 ([Fig. 7](#_bookmark28)D), 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 *Y*H2 exhibits a decreasing trend as *S* increases for Agricultural and green residues, Aquatic biomass, and Municipal waste cate- gories 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](#_bookmark114),[105](#_bookmark115)].

Total Carb.

Starch

COD

BOD

TC

TN

TP

C

H

N

569.0a 0.5a

<10-3a

569.0b 470.0b 1.0b

94.0d

29.8 5.2 5.5

133.7c

14.4c

142.0e

48.5 6.8 4.4

6e12.5g

3.6e7.5h

42.7g

12.4c

4.7 26.4

40.6g

1.6g

21.3c

55.2

55.2 0.2

0.1

Moreover, studies using different biomasses esuch as food waste [[106](#_bookmark116)], waste paper [[107](#_bookmark117)]e 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 ac- tivity, thus using a larger substrate amount than those with low hydrogenase activity [[108](#_bookmark119)]. However, using cheese whey powder as feedstock ewhich is classified in the Industrial- derived products categorye was obtained a high *Y*H2 (296.8 mL H2/g substrate) at high *S* (46.4 g/L) [[58](#_bookmark77)]. Moreover, studies that employed feedstocks from the Industrial efflu- ents category reported *Y*H2 values between 416.7 and

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

Protein Lipid Lignin

VSS DS Ash

Moist.

357.0d

1.2c

491.0e

92.4

5.2e

1.8e3.7f

84.5e92.1

78.3g

10.5g

6.2g

0.6 65.8

423.8 mL H2/g substrate at relative low *S* values (5e24 g/L) [[109](#_bookmark118)e[113](#_bookmark118)]. *Y*H2 seems to increase as *r*H2 increases in studies using biomasses of Agricultural and green residues, Industrial-derived products, and Industrial effluents cate- gories (Fig. S3B). However, when feedstocks of the Aquatic biomass category were employed as the substrate, *Y*H2 seems to decrease as *r*H2 increases. For instance, the lowest *r*H2 (14.1 mL H2/L∙h) was accompanied by a relative high *Y*H2 (339 mL H2/g) [[114](#_bookmark124)]. Also, the lowest *Y*H2 (41.4 mL H2/g) was obtained together with a relative high *r*H2 (222.8 mL H2/L∙h) [[115](#_bookmark125)]. However, a study in which microalgae was employed as feedstock [[44](#_bookmark66)] reported a high *Y*H2 (391.5 mL H2/g) with a high *r*H2 (1916 mL H2/L∙h, not included in the plot). There- fore, there is necessary more data to establish a clear rela- tionship between *Y*H2 and *r*H2 when feedstocks from the Aquatic biomass category are used.

Category Subcategory

Biomass

Solids and moisture

TS

VS

SS

Municipal Wastepaper waste

Sewage sludge

18.5c

6.4

12.0c

4.0

13.7c 12.2c

Food waste Domestic food waste 25.3

7.5e12.6

23.8

6.5e11.5

11.6e16.9 8.4e15.0

19.6g

17.8g

13.4c 10.8c

Food industry waste

34.2

98.0

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. 7](#_bookmark28)A. 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. 7](#_bookmark28)B. Concerning *r*H2, [Fig. 7](#_bookmark28)C 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 *Y*H2



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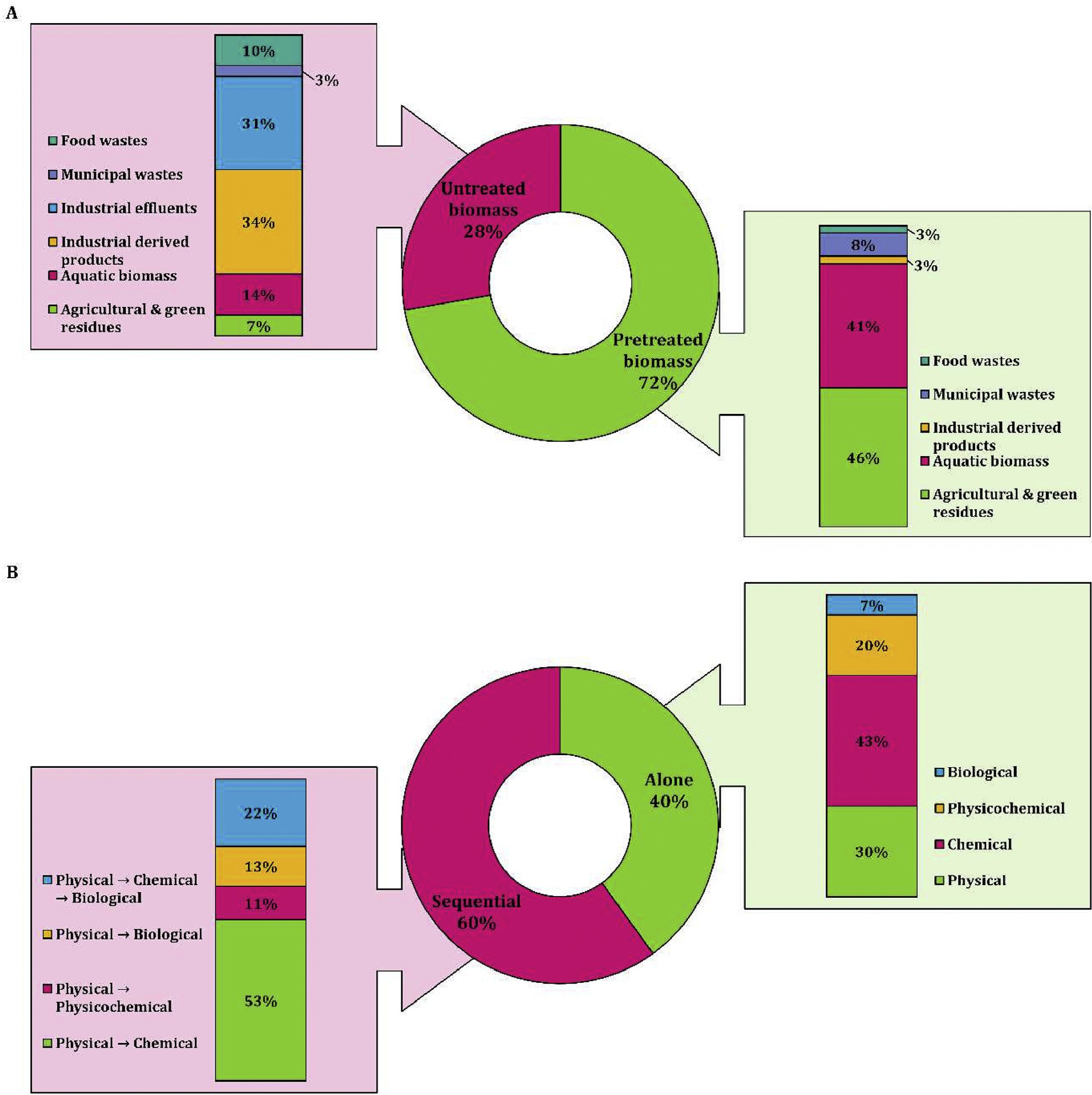


Fig. 4 e Feedstock pretreatments commonly used before dark fermentation. Untreated and pretreated biomass (A). Single and sequential pretreatments (B).

([Fig. 7](#_bookmark28)D), 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 *Y*H2 and *S* econsidering G2 datae is shown in Fig. S2B. A decreasing trend was observed in studies using biomass of Agricultural and green residues cate- gory as substrate. As previously reported, increasing substrate concentration may lead to a decrease in H2 production [[116](#_bookmark126)]. 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 2.5e37.75 g/L,

obtaining *Y*H2 > 90 mL H2/g substrate. For the rest of the feed- stocks, not enough data (*N* ≤ 2) are available in the database to describe their trend. Additionally, the *Y*H2 changes are directly

proportional to *r*H2, as shown in Fig. S3B.

*Chemometric analysis*

The colourmap for Matrix X1 (Table S2) is shown in [Fig. 8](#_bookmark29). The colourmap collects information from the dendrograms con- structed with 24 objects (*i.e.*, studied samples; Fig. S4A) in a space of 12 parameters ([Table 3](#_bookmark11)A, 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 character- ized by low *S* (4.8e16.3 g substrate/L), as well as low butyrate (BTA) concentration (0.16e3 g/L). The Sub-clusters A1 and A2 are unique due to high pH values (6.8e8.5) and high *Y*H2 values (>423 mL H2/g substrate), respectively. The colourmap shows the singularity of Object 3 due to the lowest *Y*H2 (84.73 mL H2/g substrate) as well as Object 11 due to the highest pH (8.5)



18 [i n t ern ati on a l j o u rn a l of h y dro g e n ener gy x x x ( x xxx ) x x x](https://doi.org/10.1016/j.ijhydene.2022.02.106)

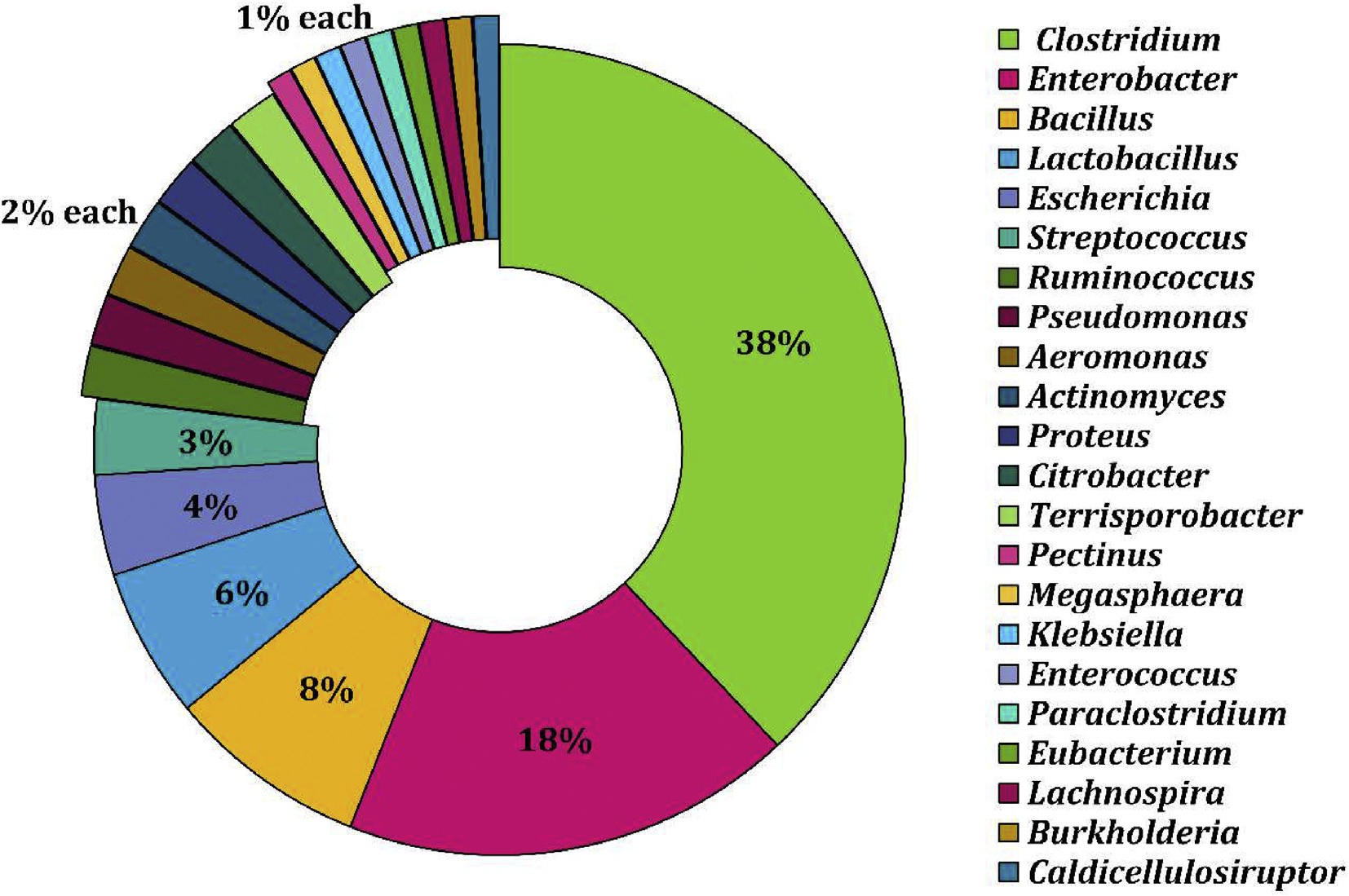


Fig. 5 e Microorganisms used or found in dark fermentation.

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

*Y*H2 (41.4e282.7 mL H2/g substrate). Sub-cluster B1 is unique

due to the high concentration of BTA (1.71e6 g/L) in compar- ison 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 e Mixed and pure cultures used/found in dark fermentation-bioreactors according to feedstock categories. | | | |
| Feedstock category | Mixed culture  Undefined | Defined | Pure culture |
| Agricultural & green residues | *Clostridium*a *Clostridium/Enterobacter*b  *Clostridium/Enterobacter/Terrisporobacter*c *Clostridium/Enterobacter/Lachnospira/Citrobacter*d *Ruminococcus*e  *Clostridium*f *Clostridium/Enterobacter*g *Clostridium/Ruminococcus*h *Clostridium/Eubacterium*i *Clostridium/Bacillus/Lactobacillus*j  *Clostridium/Enterobacter/Aeromonas/Bacillus*k *Clostridium/Bacillus/Terrisporobacter/Paraclostridium/Enterococcus/ Actynomyces*l  *Clostridium/Lactobacillus*m *Clostridium/Enterobacter*n *Clostridium/Enterobacter/Lachnospira/Citrobacter*d *Clostridium/Enterobacter/Burkholderia*o *Pectinus*/*Clostridium/Megasphaera/Lactobacillus*p  *Clostridium/Lactobacillus/Enterobacter/Streptococcus/Escherichia*q *Clostridium/Lactobacillus/Enterobacter/Streptococcus/Escherichia/ Pseudomonas/Aeromonas/Actinomyces/Klebsiella*r *Clostridium/Enterobacter/Terrisporobacter*c | *Clostridium/Bacillus*s *Clostridium/Citrobacter*t | *Clostridium*x *Enterobacter*y *Bacillus*z *Proteus* ai |
| Aquatic biomass | *Clostridium/Escherichia*u | *Clostridium*bi *Enterobacter* ci *Pseudomonas* di *Caldicellusiruptor* ei |
| Industrial derived products |  | *Clostridium*fi |
| Industrial effluents | *Escherichia/Enterobacter*v |  |
| Municipal Waste Food waste | *Enterobacter/Bacillus/Proteus*w |  |
| a[[160](#_bookmark162),[211](#_bookmark211)],b [[163](#_bookmark165),[219](#_bookmark218),[338](#_bookmark311)],c [[341](#_bookmark314)],d [[334](#_bookmark307)],e [[361](#_bookmark334)],f [[44](#_bookmark66),[135](#_bookmark141),[212](#_bookmark212),[362](#_bookmark335)],g [[48](#_bookmark70)],h [[47](#_bookmark69)],i [[115](#_bookmark125)],j [[138](#_bookmark145),[139](#_bookmark144)],k [[273](#_bookmark265)],l [[287](#_bookmark279)],m [[350](#_bookmark323)],n [[58](#_bookmark77)],o [[112](#_bookmark122)],p [[111](#_bookmark121)],q [[109](#_bookmark118)],r [[164](#_bookmark166)],s  [[134](#_bookmark140)],t [[288](#_bookmark280)],u [[220](#_bookmark219)],v [[113](#_bookmark123)],w [[284](#_bookmark276)],x [[140](#_bookmark146),[161](#_bookmark163),[162](#_bookmark164),[270](#_bookmark262),[280](#_bookmark272),[337](#_bookmark310)],y [[116](#_bookmark126),[285](#_bookmark277),[340](#_bookmark313)],z [[205](#_bookmark205)], ai [[286](#_bookmark278)], bi [[343](#_bookmark316),[346](#_bookmark319),[347](#_bookmark320)], ci [[279](#_bookmark271),[344](#_bookmark317),[345](#_bookmark318)], di [[349](#_bookmark322)], ei [[215](#_bookmark214)], fi [[204](#_bookmark204)]. | | | |



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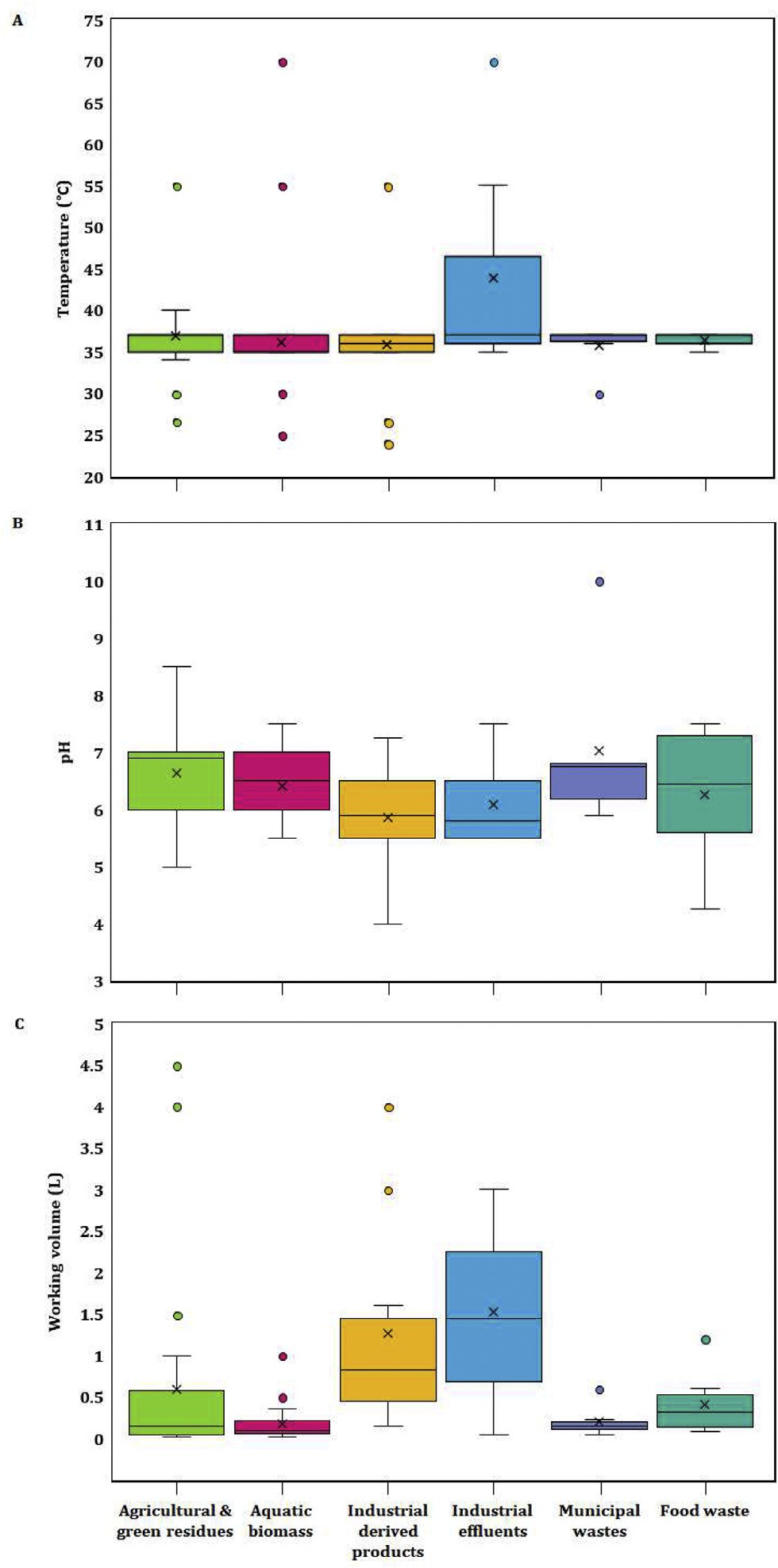


Fig. 6 e Temperature (A), pH (B) and working volume (C) used for hydrogen production *via* dark fermentation according to the feedstock employed.

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 *r*H2 (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](#_bookmark30). 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, 5e9, 12, 13, 15e17 and 21) is char- acterized by low H2ac (107.5e1079 mL H2/L) and *Y*H2 (4.6e77.2 mL H2/g substrate). Sub-cluster D1 (objects 2, 5, 7, 8, 13 and 17) exhibits a relatively high pH (6.5e7) in comparison with the rest of the Objects. The Objects collected in Sub- cluster D2 were identified by the lowest *Y*H2 (8.96e55 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* (40e43 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 *Y*H2 (168.6e219.67 mL H2/g substrate) compared with the rest of the Objects. Object 1 within sub-cluster E1 is singular by the highest *Y*H2 (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 con- centration 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 (2e8.83 g/L and 2.33e13.22 g/L, respectively). Sub-cluster F1 is additionally distinguished by a high concentration of EtOH (0.42e0.47 g/L). The highest concentration of EtOH is observed in Object 14. The highest *r*H2 (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 VW (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 *r*H2 values are related to both 6 ≤ pH ≤ 6.8 and 35 ◦C ≤ T ≤ 37 ◦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

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 Ob- jects are particular due to the relatively high Vw (1.5e3 L) and concentration of lactate (LA, 1.49e7 g/L). Sub-cluster C1 (objects 4, 20 and 21) is additionally characterized by relatively high T (55e70 ◦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 VW, 1.6 and 3 L, respec- tively. Further, the uniqueness of Object 16 could be observed, mainly due to the lowest T and *Y*H2 e24 ◦C and 99.73 mL H2/g substratee and relatively low value of pH (5.1) in comparison

related to low *r*H2 as showed by Sub-cluster B2. In addition, high *Y*H2 are related to mesophilic conditions as well as

5.5 ≤ pH ≤ 7.5 (see Sub-cluster A2 and Cluster E). Although

thermophilic conditions may lead to high *Y*H2 values, an appropriate combination of T and pH should be used. Other- wise, *Y*H2 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 *Y*H2. This can be observed in both Sub-cluster A2 and Cluster E, which obtain high values of *Y*H2 at low levels of *S*. High levels of *S* might lead to the accumu- lation 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.



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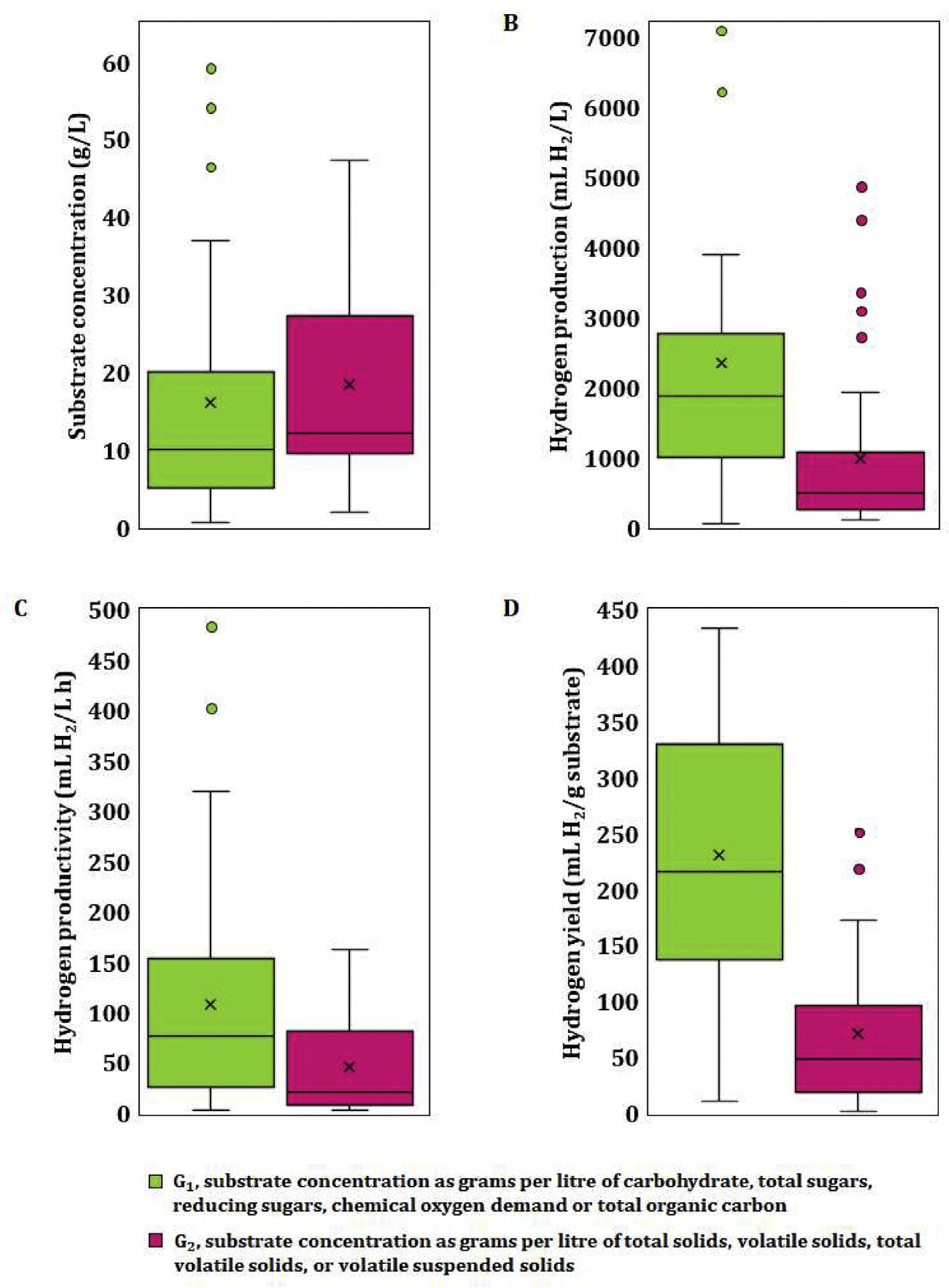


Fig. 7 e Dark fermentation performance. Substrate concentration (A), hydrogen production (B), hydrogen productivity (C) and hydrogen yield (D) reported in studies from the database.

Additionally, the balance of NADþ/NADH is modified, thus decreasing metabolic activity and leading to enzymes inacti- vation involved in H2 production [[117](#_bookmark127),[118](#_bookmark128)]. Moreover, H2 par- tial pressure may also be influenced by *S*, which is related to inhibitory effects on the performance of DF [[119](#_bookmark129),[120](#_bookmark130)].

[methods](#_bookmark19) and Section [Hydrogen-producing microorganisms](#_bookmark20). The most abundant by-products ewith amounts >2 g/Le identified with the HCA were AcOH, LA, EtCO2, BTA, and EtOH. AcOH, LA, BTA, and EtOH are metabolites associated with hydrogenic bacteria [[83](#_bookmark94),[121](#_bookmark131),[122](#_bookmark132)]. EtCO2 can be a metabolite in some H2-producing systems as well. However, propionic fer-

menters must be avoided in DF since they can consume H2

# By-products of dark fermentation

The by-products of DF, shown in [Fig. 10](#_bookmark31)A, are a mixture of VFAs and solvents ([Fig. 11](#_bookmark32)). These fermentative metabolites are related to the operational conditions (T, pH, *S*) and starter culture, as explained in Section [Feedstock pretreatment](#_bookmark19)

and/or reduce equivalents [[67](#_bookmark83),[123](#_bookmark133)]. 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.



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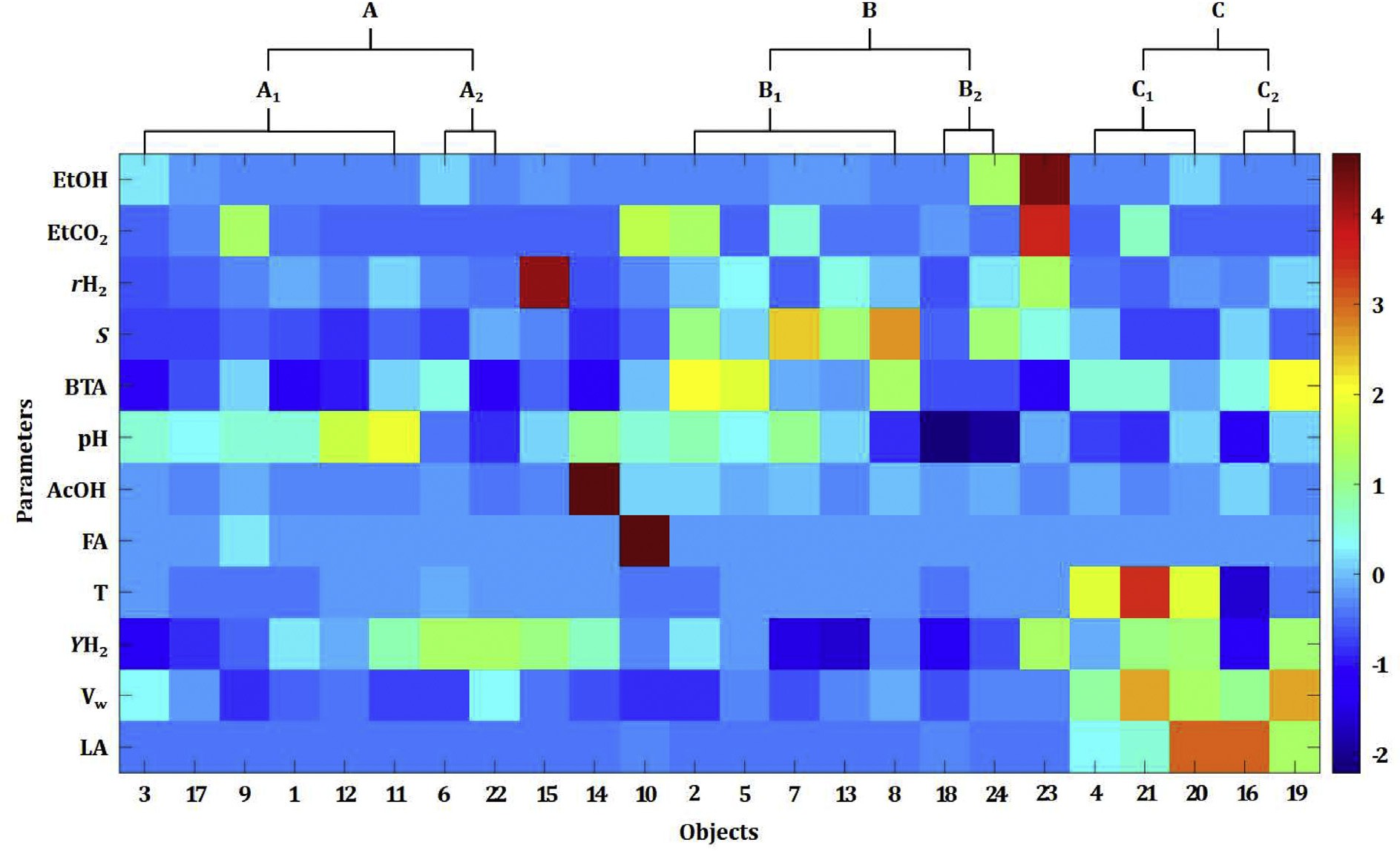


Fig. 8 e Colourmap of the studied data (Matrix X1) demonstrating the values of the measured parameters for measuring points.

*Acetic acid*

AcOH (C2H4O2 or CH3COOH) is one of the most important chemicals with increasing global demand (16e18 million tonnes in 2020) [[129](#_bookmark135),[130](#_bookmark136)]. 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](#_bookmark135),[131](#_bookmark137)]. 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](#_bookmark138)]. Currently, AcOH is

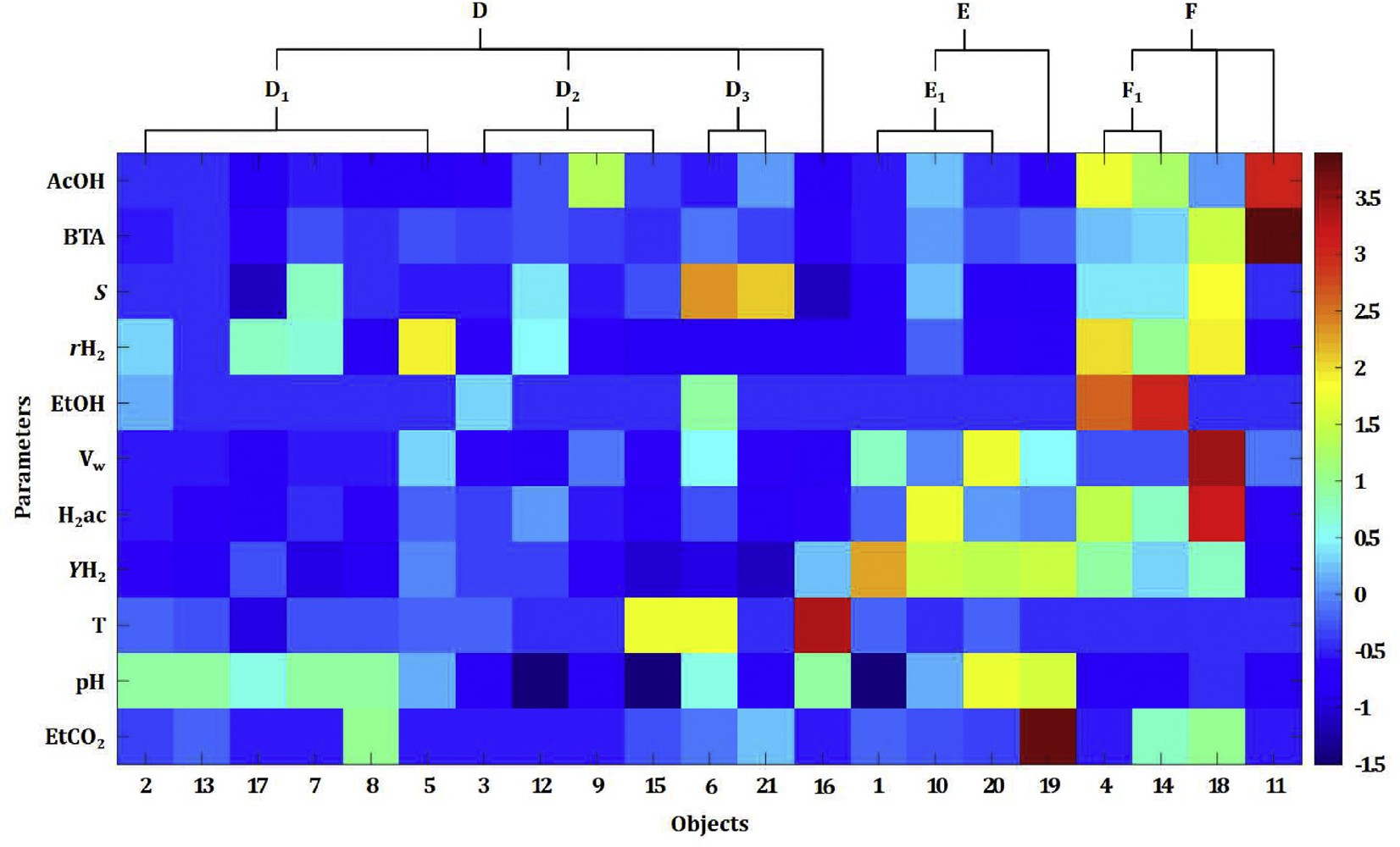


Fig. 9 e Colourmap of the studied data (Matrix X2) demonstrating the values of the measured parameters for measuring points.



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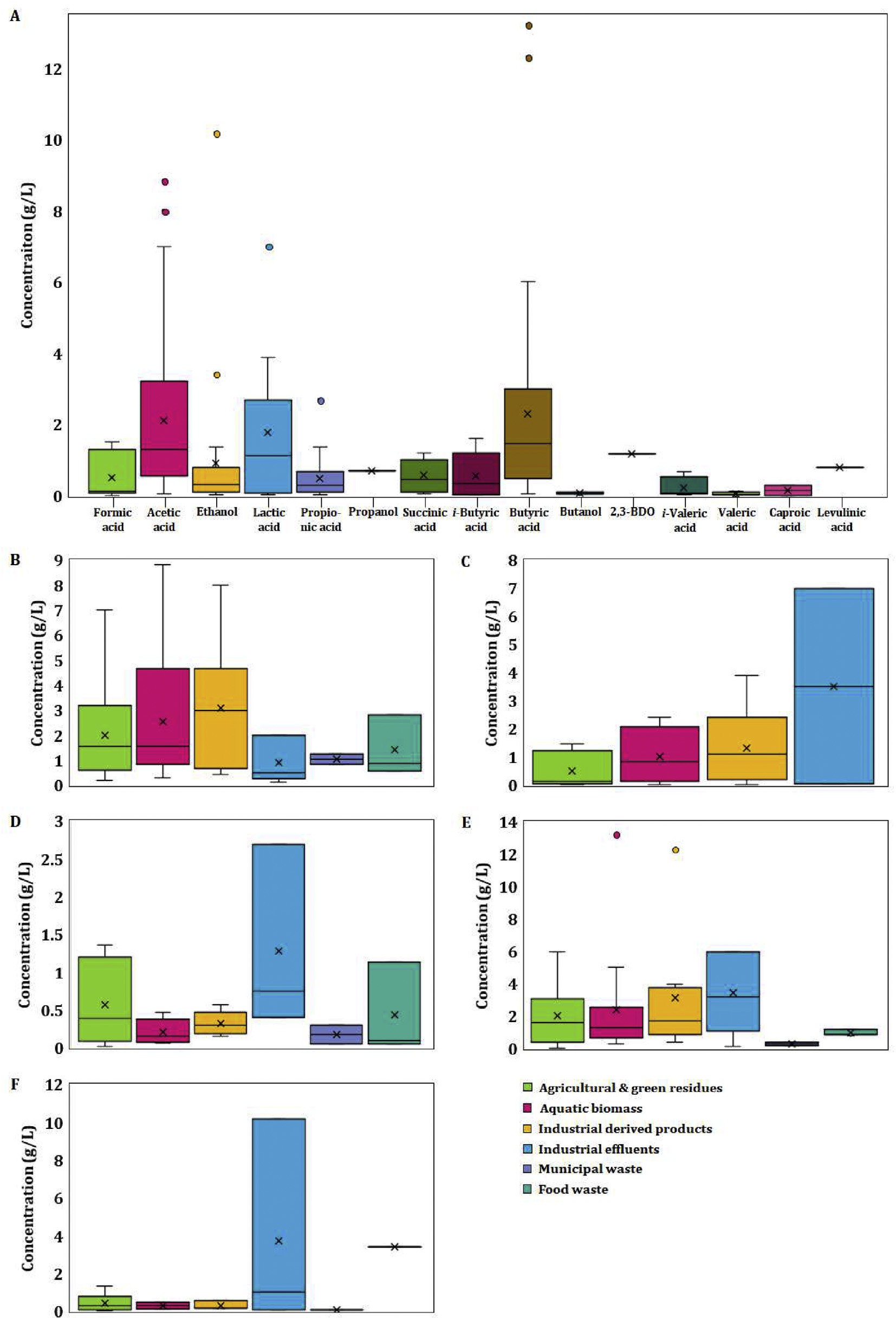


Fig. 10 e By-products generated during hydrogen production *via* dark fermentation (A). Acetic (B), lactic (C), propionic (D), butyric (E) acids, and ethanol (F) production as a function of feedstock employed.

mainly produced through carbonylation of methanol and oxidation of ethylene or acetaldehyde [[131](#_bookmark137),[133](#_bookmark139)]. 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 be- tween 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



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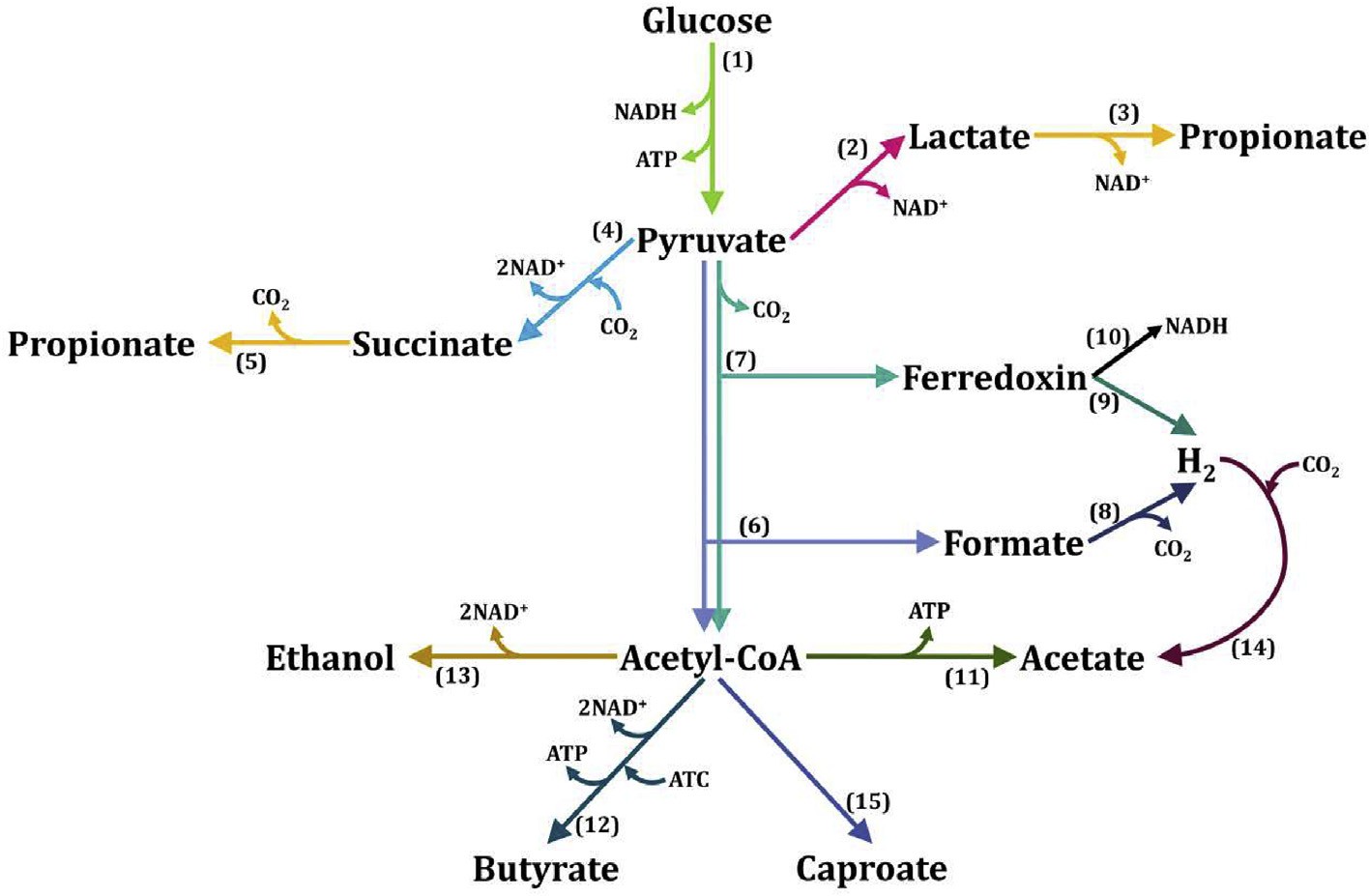


Fig. 11 e Main catabolic pathways in acidogenic glucose fermentation, adapted from Refs. [[124](#_bookmark134)e[128](#_bookmark134)]. Reaction (1) illustrates the formation of pyruvate from glucose. NADH produced [reaction (1)] should be reconverted to NADþ. One way is through the production of lactate 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 NADþ. 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 NADþ 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 *Y*H2 (Object 9 of Sub-cluster D2, Object 11 of Cluster F), as shown [Figs. 8 and 9](#_bookmark29). The highest concentrations (≥7 g/L) of AcOH were produced using biomass from Agricul-

tural and green residues, Aquatic biomass, and Industrial-

derived products categories ([Fig. 10](#_bookmark31)B). 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), fol- lowed by BTA (1.8 g/L), succinate (1 g/L), and EtOH (0.4 g/L) [[134](#_bookmark140)]. 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](#_bookmark141)]. The DF, using an undefined mixed culture, of cheese whey produced a mixture of VFAs con- formed by AcOH (8 g/L), BTA (4 g/L), *i*-butyrate (0.77 g/L), and EtCO2 (0,25 g/L) [[136](#_bookmark142)]. 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 4e6 g/L [[137](#_bookmark143)e[140](#_bookmark143)].

Recent research has been focusing on improving the pro- duction 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](#_bookmark147)]. Further, the co-culture of *C*. *thermosacchar- olyticum* 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](#_bookmark148)]. In addi- tion, 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](#_bookmark149)]. 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 micro- flora was abundant in AcOH-producing *Enterococcus* (54.1%), followed by H2-producing bacteria affiliated to *Enterobacteri- aceae* (27.5%) and *Clostridium* (5.1%) [[144](#_bookmark150)]. 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



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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](#_bookmark151)e[147](#_bookmark151)]. 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](#_bookmark152)]. Most commercial production of LA is by microbial fermentation of carbohydrates, its price reaching around 3.0e4.0 USD/kg and is expected that its demand will reach ~2.0 million tonnes in 2025 [[149](#_bookmark153)].

LA was produced in studies employing biomass from the following categories as feedstock: Agricultural and green res- idues (0.05e1.49 g/L), Aquatic biomass (0.02e2.4 g/L), Industrial-derived products (0.02e7 g/L), and Industrial efflu- ents (0.05e7 g/L) ([Fig. 10](#_bookmark31)C). HCA established that studies grouped in Cluster C are characterized by high LA concen- trations. 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](#_bookmark68)]; 0.55 g/L, *S*: 10 g VS/L [[47](#_bookmark69)]), cheese whey (7 g/L, *S*:

20 g lactose/L [[150](#_bookmark154)]), wheat starch (3.89 g/L, *S*: 3.6 g COD/L [[151](#_bookmark155)]), and sugarcane vinasse (7 g/L, *S*: 5.02 g carbohydrate/L [[110](#_bookmark120)]) as substrate. However, reduced end products such as LA must be avoided during DF to maximise *Y*H2 values, since its presence represent H2 that was not released as a gas [[66](#_bookmark82),[120](#_bookmark130)].

### 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 cel- lulose acetate propionate and vitamin E, as well as an esteri- fying agent in thermoplastics production and flavours and perfume bases manufacture. The global EtCO2 production was estimated at approximately 450,000 tonnes per year with 2e3 USD/kg as selling price [[152](#_bookmark156)]. EtCO2 is mainly produced by petrochemical processes such as oxidation of propanol or propanal, hydrolysis of esters, and hydrocarboxylation of ethylene [[152](#_bookmark156)e[154](#_bookmark156)].

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. 10](#_bookmark31)D). 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 (1.1e2.7 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 demon- strated that VFAs production at thermophilic conditions is lower (40%) than mesophilic conditions [[155](#_bookmark157)]. Likewise,

optimal pH for the production of a specific VFA is highly dependent on the type of feedstock employed [[156](#_bookmark158)]. EtCO2 production from wastewater is favoured at a pH of 4e4.5, whereas for AcOH and BTA, a pH of 6e6.5 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](#_bookmark157),[156](#_bookmark158)]. However, high *Y*H2 values are usually associated with BTA production and low production of EtCO2 and reduced end products (*e.g.*, alcohols, LA) [[120](#_bookmark130)].

### 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 hemoglobinop- athies, 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](#_bookmark159)e[159](#_bookmark159)]. 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 (0.04e6 g/L), Aquatic biomass (0.03e13.2 g/L), Industrial derived products (0.4e13.2 g/L), In- dustrial effluents (0.16e6 g/L), Municipal wastes (0.17e0.4 g/L), and Food wastes (0.85e1.17 g/L), as shows [Fig. 10](#_bookmark31)E. 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 *Y*H2 (Objects 11 and 14 of Cluster F). Additionally, BTA production is usually accompanied by AcOH (Sub-cluster B1, Clusters C and F). *Clos- tridium* strains have been recognized by achieving high pro- duction 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](#_bookmark162)], carob pulp [[161](#_bookmark163)], corn stalk [[162](#_bookmark164)], rice husk [[163](#_bookmark165)], algal bloom [[135](#_bookmark141)], co-culture of tequila vinasses and nixtamalization wastewater [[109](#_bookmark118)], and tequila vinasses [[164](#_bookmark166)], to produce BTA as the main by-product of DF in amounts of approximately 5e13 g/L. Also, using seaweed and wheat bran was produced BTA in high amounts (5e12 g/L) but information of the microbial community employed is not provided [[165](#_bookmark167),[166](#_bookmark168)].

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](#_bookmark83),[101](#_bookmark111)]. Nevertheless, controlling the

buffering system (NaOH þ CaCO3), BTA production was

enhanced (almost 3-fold) during DF using food waste as sub- strate [[167](#_bookmark169)]. 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](#_bookmark170)]. In addition,



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optimization of the conditions of pH (7) and T (35 ◦C) eusing 80

or 100 g VS/L of microalgae as substratee, generates high yields of H2 (22 mL H2/g VS) and BTA (0.05 g/g VS) [[169](#_bookmark171)]. 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](#_bookmark160)].

### 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 (106e110) than gasoline's (91e96) [[170](#_bookmark172),[171](#_bookmark173)]. EtOH (biofuel) production reached 110 billion L globally in 2018 and is anticipated a 20% increase by 2024 [[172](#_bookmark174)].

EtOH concentration average of 0.9 g/L was found in the research articles included in the database, as shown in [Fig. 10](#_bookmark31)F. 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 feed-

stock, EtOH is the main metabolite and appears in concen- trations of 10 g/L [[113](#_bookmark123)] and 3.4 g/L [[173](#_bookmark175)], respectively. Although EtOH is not the target product in DF, EtOH production seems to be favoured at mesophilic conditions and pH approximately of 4.2e6.3 (Object 24 of Sub-cluster B2, non-clustered Object 23 of Matrix X1, Objects 4 and 14 of Cluster F). Further, EtOH pro- duction 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 eunder meso- philic and/or thermophilic conditionse the metabolic flux favours the AcOH and BTA production instead of EtOH [[109](#_bookmark118),[111](#_bookmark121),[164](#_bookmark166)]. 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](#_bookmark123)]. Both *Escherichia* and *Enterobacter* strains produce H2 and EtOH from glycerol under anaerobic conditions [[174](#_bookmark176)e[176](#_bookmark176)].

EtOH concentration must be >4% (w/w) for a profitable

separation using distillation [[177](#_bookmark177)]. Considering the titters ob- tained in DF (average of 0.9 g/L, according to database), EtOH production by mixed-cultures is neither economic nor ener- getically competitive compared with corn- and sugarcane- based EtOH [[178](#_bookmark178)].

### Challenges for industrial production of bio-based chemicals

Bio-based chemicals production is an alternative to the renewable production of chemicals building blocks. Notwith- standing, 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 50e100 g/L, production rates of 1e3 g/L$h, and yields >0.5 g/g are required [[159](#_bookmark161),[179](#_bookmark179)]. 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](#_bookmark180)], low-cost purification processes have not been developed yet for AcOH, BTA and EtCO2 [[178](#_bookmark178)]. The recovery of individual VFAs is even more difficult than of VFAs mixtures [[181](#_bookmark181)]. So far, technologies used for VFAs recovery after the fermentation stage from broths include gas stripping with absorption [[182](#_bookmark182),[183](#_bookmark183)], adsorption [[184](#_bookmark184),[185](#_bookmark185)], electrodialysis [[186](#_bookmark186),[187](#_bookmark187)], sol- vent extraction [[188](#_bookmark188),[189](#_bookmark189)], nanofiltration [[190](#_bookmark190)], reverse osmosis [[191](#_bookmark191)], and membrane contactors [[192](#_bookmark192)]. However, *in-situ* re- covery of VFAs, which can either be carried out continuously or intermittently during fermentation [[193](#_bookmark193)] can also prevent product-inhibitory effects as well as VFAs consumption dur- ing internal conversion reactions [[181](#_bookmark181),[193](#_bookmark193),[194](#_bookmark194)]. The *in-situ* recovery of VFAs can also increase VFAs production rates [[195](#_bookmark195)], extraction yields [[196](#_bookmark196)], extraction efficiency [[197](#_bookmark197),[198](#_bookmark198)], as well as the reduction of carbon footprint [[199](#_bookmark199)].

Further research is required to develop profitable produc-

tion and recovery methods. Besides, a deeper understanding of microbial communities and their interactions with VFAs production pathways will be fundamental to achieving prof- itability [[181](#_bookmark181),[200](#_bookmark200)].

### 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](#_bookmark201)e[205](#_bookmark201)]. To be sustainable, DF must be integrated into biorefining strategies with bioenergy or value-added co-products as their outputs ([Fig. 2](#_bookmark12)A).

A biorefinery scheme including a DF stage followed by anaerobic digestion (AD) stage might 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 *Meth- anoculleus* sp.) to produce CH4 [[206](#_bookmark206)]. The final product of this

sequential two-stage process is called bio-hythane (H2 þ CH4),

with an overall fermentation time of 13e18 days. Bio-hythane production in a two-stage process can improve energy re- covery and reduce fermentation time. Further, the separation of AD from DF provides good control of microbial commu- nities with different functions [[207](#_bookmark207),[208](#_bookmark208)]. 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](#_bookmark209)]. Using sugarcane tops in a similar system, an energy recovery of 7.07 MJ/kg VS was achieved [[210](#_bookmark210)]. 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](#_bookmark211)]. Biomass from microalgae [*Chlorella* sp., microalgae



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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](#_bookmark125),[135](#_bookmark141),[139](#_bookmark144),[212](#_bookmark212)e[215](#_bookmark212)]. 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](#_bookmark167)]. Since H2 is a carbon-free fuel, its combination with CH4 may contribute to reducing CO2 and NOx emissions to the atmosphere [[216](#_bookmark215)]. Despite several advantages of bio-hythane production, chal- lenges related to metabolic pathways, reactor configuration, recycling of digestate, and physicochemical parameters must be addressed before scaling up for commercial production [[202](#_bookmark203),[217](#_bookmark216)]. 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) esuch as *Rhodopseudomonas palustris*, *Rhodobacter sulfidophilus*, *R. capsulatus*e can metabo- lize organic acids (*e*.*g*., acetate, butyrate, succinate, lactate) and produce H2 and CO2 using light as an energy source [[218](#_bookmark217)]. 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](#_bookmark218)]. 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](#_bookmark219)]. *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](#_bookmark220)]. *Arthrospira 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](#_bookmark145)]. The combination of DF and PF seems a promising strategy for H2 production since integrated systems may improve the H2 yields and en- ergy recovery. However, the theoretical H2 yield (12 mol/mol glucose) of the integrated system has not been achieved yet [[222](#_bookmark221)]. 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 inter- mediate step will increase CAPEX [[223](#_bookmark222)]. Despite VFAs con- sumption 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](#_bookmark145),[224](#_bookmark223)].

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](#_bookmark224)]. The integration of DF with MEC has been recognized as a promising method to convert biomass into H2. Integrated systems increased H2 yields eusing feedstock such as POME, vinasses, sugar beet juicee compared with a single DF stage system [[226](#_bookmark225)e[229](#_bookmark225)]. However, using fermentation effluents as substrate, the H2 production rate can be decreased

and a substantial amount of methane can be produced [[230](#_bookmark226)]. Limitations such as low energy efficiencies, competing re- actions (*i.e.,* methanogenesis), growth of H2 scavengers, among other factors, must be avoided before increasing the capacity of MECs to industrial scales [[231](#_bookmark227)]. 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](#_bookmark228)]. The general pathway of lipid synthesis from glucose involves its conversion to acetate and then its channelization to lipogen- esis. However, some oleaginous microorganisms can use VFAs as the sole carbon source to accumulate lipids [[233](#_bookmark229),[234](#_bookmark230)]. 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](#_bookmark231)]. Duckweed biomass was used as feed- stock for DF and *C. sacchrarophila* cultivation. As a result, microalgal growth and lipid production were promoted by using DF effluents as feedstock [[94](#_bookmark104)]. Effluents from DF of molasses were also employed as feedstock for lipid produc- tion. Coupling DF with the cultivation of *Scenedesmus* sp., 97.3% additional energy was produced compared with DF alone [[236](#_bookmark232)]. DF coupled with lipid production by *Rhodotorula minuta* improved the energy recovery as compared with a single-stage process [[204](#_bookmark204)]. Also, the ECE was enhanced from 10% to 24% using DF coupled with algal lipid production using food waste as feedstock [[27](#_bookmark54)]. 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 down- stream processing costs, as well as increasing microbial lipid productivity [[237](#_bookmark233),[238](#_bookmark234)].

Emerging research is focusing on the use of DF residues to

produce polyhydroxyalkanoates (PHAs). PHAs are bio- polymers synthesized by microorganisms as lipid inclusions for energy storage in granular forms within the cellular structure [[239](#_bookmark235),[240](#_bookmark236)]. Microorganisms capable to produce PHAs include, but not exclusively, *P. resinovorans*, *P. aeruginosa*, *P. putida*, *P. fluorescence*, *B. cereus*, and *Lysinibacillus sphaericus* [[241](#_bookmark237)]. The VFAs in DF effluents can act as a carbon source for microbial growth as well as precursors for biopolymers pro- duction (acetate for hydroxybutyrate, propionate for hydrox- yvalerate, butyrate for hydroxyhexanoate) [[239](#_bookmark235)]. Renewable feedstock such as wastes from dairy industries [[242](#_bookmark238)], hydro- lysed polyacrylamide-containing wastewaters [[77](#_bookmark90)], giant cane biomass [[243](#_bookmark239)], has been used in a system combining DF and PHAs production, obtaining approximately 1.4e2 mol H2/mol sugars and 54e62 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 simulta- neous H2 and PHAs production combining DF by *B. cereus* and PF by *R. rutila*, obtaining approximately 1.6e1.8 mol H2/mol sugars and 10e19 g/L PHAs [[205](#_bookmark205)]. H2 is a clean and renewable energy source that may substitute fossil fuels, and PHAs are



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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](#_bookmark240),[245](#_bookmark241)]. 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](#_bookmark242)]. 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 *Y*H2. H2 production by SSF using microalgae as substrate has already achieved *Y*H2 < 20 mL H2/ g VS [[247](#_bookmark243),[248](#_bookmark244)]. Rice husk was also subjected to SSF with a co-

culture of *C. termitidis* and *C. intestinale* (5:1) at 37 ◦C and

30 rpm. The *Y*H2 was 5.9 mL H2/g substrate [[249](#_bookmark245)]. Further, ground wheat was used with *C. acetobutylicum* at mesophilic conditions achieving 63 mL H2/g starch [[250](#_bookmark246)]. During SSF, the availability of water decreases due to its adsorption onto the biomass, leading to higher concentration of inhibitory com- pounds [[246](#_bookmark242)]. Moreover, high TS content is related to low mass transfer rates, which may induce unfavourable conditions to biological reactions [[246](#_bookmark242)]. 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 sus- tainable 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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