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A critical review on biofilm-based reactor systems for enhanced syngas fermentation processes

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ABSTRACT

For encouraging industrial growth based on sustainability, renewable energy sources as replacement of fossil fuels have gained a great importance worldwide. Syngas fermentation fulfills the requirements for sustainable bioenergy and biochemical productions. In comparison to other gas to biofuel conversion methods such as Fischer-Tropsch synthesis, it not only requires less energy owing to its low operating temperature and pressure, it also offers greater flexibility in terms of feedstock composition as well as variety of the end products. In addition, biological catalysts are capable of adopting presence of impurities in syngas whereas metal catalysts get deactivated. Lanzatech has successful commercial plants in operation utilising the CO rich off gas from the steel industry. However, low mass transfer rate in the gas-liquid interface is the major obstacle which renders widespread adoption and industrial applications of the process limited. Recent research data indicates the capability of the biofilm reactors on improving mass transfer rates as well as achieving greater process stability. This review collates the literature on impact of biofilm technology to provide new insights in syngas fermentation to guide future research towards commercialisation of renewable sustainable biofuels and biochemicals. In this regard, operation principles, economic perspectives and mass transfer mechanisms of various biofilm reactors are compared among each other as well as with the conventional reactor configurations. Current commercialisation stage of syngas fermentation is summarised along with pilot scale patent as the initiatives of future plants. Overall, operation challenges from both microbial and bioprocessing standpoint are highlighted, and potential solutions are provided.

1. Introduction

Last few decades have witnessed an enormous rise in global energy demand as a result of increased population as well as growing industrialisation. The world population is expected to grow over 8 billion by 2030 [1]. As a result of swift industrialisation and population growth, an approximately 50% increase in global energy demand has been estimated by 2030 [2]. The global liquid fuel demand for transportation is estimated to increase by 27.4% of 2015 levels reaching 121 million barrels per day by 2040 correspondingly [3]. Currently, approximately 80% of worldwide energy demand is fulfilled by utilising fossil fuels [1,4] which are estimated to be extinct within 50 years based on recent consumption rates [5]. Apart from the depletion risk of the fossil fuels, majority of the crude oil reserves are located in economically and politically unstable regions causing continuous fluctuations in the global supply chain as well as the pricing [1]. However, the biggest challenge the mankind facing is the tremendous levels of greenhouse gas (GHG) emission, particularly CO_2 causing, global climate change arising from the widespread use of fossil fuels [6,7]. Necessity of exploring alternative energy sources was established due to the increasing global demand as well as the environmental and the economic concerns. In this regard the European Union has set a target of reducing the GHG emission by 80–95% by 2050 with regard to 1990 levels [8].

In order to meet this target "biomass to bioenergy" conversion technologies are considered to be promising in terms of creating a circular economy. Early research attempts went into 1st generation biofuels where food resources such as starch, corn, vegetable oil, sugarcane, canola, sunflower, rapeseed are used as feedstock of the process [9]. For instance the global bioethanol production is mainly rely on corn (US), sugar cane (Brazil), canola and sunflower (Europe) [10,11]. At the same time, 16.67% of the world population live in hunger which corresponds to a larger population than the EU, US, Canada and Russia [12]. In addition, 1st generation biofuel production is directly linked to the intense agricultural land use as well as impaired biodiversity [13]. As such the first generation biofuels were aimed to capped at 7% within the EU by 2030 by Renewable Energy Directive II [14]. Limitations on sustainability of the first-generation biofuels has eventually drawn

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Nomenclature

CSTR	Continuous stirred tank reactor
EPM	Extracellular polymeric matrix
FTS	Fischer-Tropsch Synthesis
GHG	Greenhouse gas
GLMT	Gas-liquid mass transfer
HFMBR	Hollow-fibre membrane biofilm reactor
HRT	Hydraulic retention time
kLa	Volumetric mass transfer coefficient
MBfR	Membrane biofilm reactor
MBR	Monolithic biofilm reactor
RPBR	Rotating packed bed biofilm reactor
TBR	Trickle bed reactor
WGS	Water gas shift

attention to the lignocellulose derived 2nd generation biofuels. Agricultural residues, energy crops, organic wastes, woody by-products are known to be main lignocellulosic biomass offering advantages like valorisation of waste residues, use of rural region in comparison to the feedstocks of the 1st generation biofuels [15,16].

Main manufacturing technologies of the 2nd generation biofuels are outlined in Fig. 1. In the biochemical conversion methods like anaerobic digestion [17], ethanol [18], butanol [19,20] and dark fermentation [21], complex organic matter is initially broken down to their monomers by enzymatic attacks then fermented into biofuels, organic solvents and value added chemicals at around ambient temperatures. The hydrolysis step is known to be the rate limiting step for biological conversions of the lignocellulosic matter as highly recalcitrant lignin and crystalline structure of cellulose consisting more than 50% of a typical lignocellulosic biomass [10,22,23]. Therefore a pre-treatment step to mitigate the structural obstacles present at the molecular level is required prior to the biochemical conversion technologies [24]. Despite implementation of the pre-treatment step, a full lignin conversion cannot be achieved. On the other hand, thermochemical technologies including biomass to liquid (pyrolysis, liquefaction) as well as biomass to gas (gasification) intermediate conversion which are subsequently transformed to bio-oil, hydrocarbon fuels and syngas (mixture of CO, CO_2 and H_2) under high temperature and pressure achieves the full conversion of the lignocellulosic biomass owing to its operational conditions [25].

The syngas fermentation process is considered to be advantageous among the biological conversion technologies as it subjects the gaseous mixture (CO, CO_2 and H_2) to fermentation directly which eliminates the additional pre-treatment step [3,24,26,27]. Therefore, the exhaust gases can directly be used as the feedstock of the syngas fermentation processes for biofuel production [28,29]. Furthermore, syngas fermentation process (Fig. 1) can be an alternative to Fischer-Tropsch Synthesis (FTS) which is a thermochemical conversion technology traditionally employed to utilise the syngas generated by gasification for the biofuel production. In fact, combining gasification with syngas fermentation as an alternative to FTS is considered be superior due its greater operational flexibility in terms of CO/H_2 molar ratio of the feedstock [30,31] and the variety of the end products including biofuels such as ethanol, butanol, hydrogen as well as organic acids like acetic acid. In addition, combining biomass gasification with syngas fermentation, as opposed to with FTS, is more cost effective as it does not require gas conditioning due to the microbial capability to adapt the impurities present in syngas such as sulphur and CO_2 [32] as well as greater fuel conversion yields at lower operation temperature [30]. Principles of syngas fermentation along with the biochemical reactions are discussed in detail in Section 2.

Syngas fermentation recently attracting more research interest due to various inherent merits. As such, it can directly be implemented to industry where the high levels of exhaust gases are constantly being released i.e steel manufacturing, oil refining and petrochemistry industry [28]. Moreover, electrochemical syngas generation is also considered to be a sustainable way of suppling feedstock for the fermentation [33]. Most importantly, creating a hybrid conversion technology by integrating gasification with syngas fermentation brings the advantages of the thermochemical (full conversion of the lignocellulosic biomass) and the biochemical (flexibility in CO/H_2 ratio of the substrate and end products) technologies together as well as eliminating a complex pre-treatment step along with high enzyme and operational cost of biomass valorisation [34]. Direct implementation of syngas fermentation to the industry with high exhaust gas emissions as well as its combination with gasification is a promising technology in term of mitigating global warming and fulfilling increased liquid fuel demand particularly in transportation front.

The current syngas fermentation processes, on the other hand, have challenges to overcome such as bacterial biomass washout, low gas solubility and mass transfer rates in the gas-liquid interface which is commonly associated with the volumetric mass transfer (k_La) value. Decency of the k_La value on gas flowrate, gas bubble size, different agitation configurations speed have been investigated on conventional bioreactor such as continuous stirred thank reactor (CSTR) where the gaseous substrate sparged through the medium [5,35–37]. Most of these methods however demand an increased agitation power input per unit area to boost microbial activity in the interfacial surface area or excessive shear stress to the microorganisms leading a further increase in the operational costs. As such it brings limitations to the full-scale applications due to high energy, infra cost demand and process stability [38]. Biofilm reactors, where the bacteria is attached to a surface and gaseous

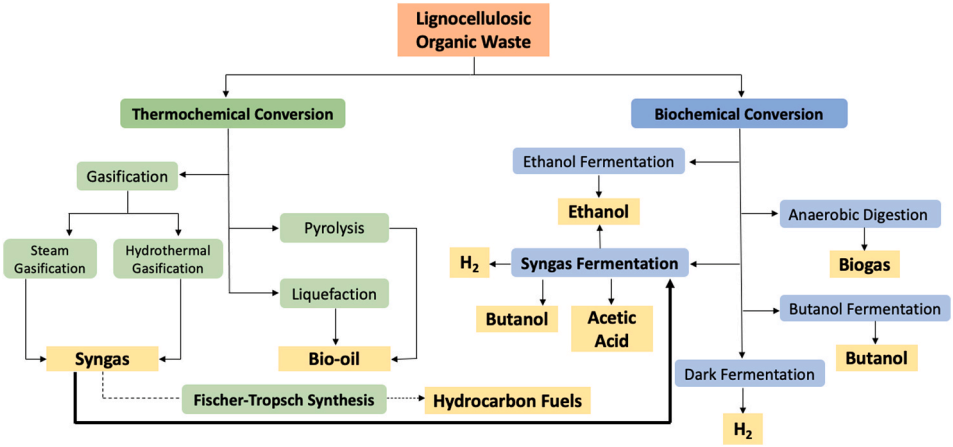

Fig. 1. Summary of key waste to energy conversion pathways adopted from [1].

substrate is transferred through the biofilm cells, are widely accepted as a promising technology in terms of addressing the limitation like shear stress and high energy input and increasing mass transfer rate in gas-liquid interface at the same time [39,40]. In a typical biofilm-based catalysis, formation of the biofilm strictly relies on adequate levels of signal cascade regulated by the intracellular secondary messenger known as bis-(3′-5′)cyclic dimeric guanosine monophosphate. In biofilm embedded bioprocesses, achieving a homogeneously organised 3D structure where the microbes are attached within an extracellular polymeric (EPM) matrix provides a long term biocatalyst stability [41,42]. EPM is particularly important in terms of providing scaffolds which stimulates bacterial cells to create synergistic microconsortia, enhances retention time and nutrient sorption from the medium while protecting cells from antimicrobials, predation and potential toxic impurities. The principles of the biofilm formation mechanism is explained in detail by Ercan [43]. Furthermore, the bacterial cell leakage phenomenon of the conventional reactors is also resolved in biofilm applications due to microbial immobilisation and separation from the liquid phase [44,45].

2. Fundamentals of syngas fermentation

In the process of syngas fermentation, acetogenic bacteria converts syngas (CO, CO_2, H_2) with flexible molar ratios to biofuels (mainly ethanol, butanol, hexanol, methane) and valuable biochemicals such as short (acetic acid, formic acid) and medium chain (caproate, caprylate) organic compounds as well as biopolymers at near ambient temperature under anaerobic conditions [3,12,46–48]. In addition, production of a gaseous fuel (H_2) is possible through water gas shift (WGS) reactions in the syngas fermentation processes.

Although it is a relatively new technology, it is well accepted due to its flexible and inexpensive nature with regard to other thermochemical conversion technologies of the syngas such as FTS. In FTS, syngas with a H_2:CO molar ratio within the range of 2:1 to 3:1 is converted to ethanol and butanol by using metal catalysts like Co, Fe, Ni and Ru [49] under high temperature (200–350 °C) and pressure (1.5–4 MPa) [50]. Furthermore, deactivation of the metal catalysts is a common operational problem seen in FTS due to the trace amounts of sulphur particularly in form of H_2S in the syngas [1]. Therefore, use biological catalysts renders the syngas fermentation processes more advantageous owing to its i: high enzymatic specificity which results in enhanced product yields [37], ii: flexibility on syngas composition [47], iii: greater ability to tolerate presence of the trace amounts of contaminants like sulphur and chlorine [51], vi: ambient operation temperature corresponds to much lower operational costs [52], (v) achieving wider range of end products due to the implementation of mixed cultures [53,54].

Syngas fermentation yields strictly relies on the metabolic activity of the microbes involved in two main stages known as acetogenesis and solventogenesis where acetogenic bacterial growth, fatty acid production and fatty acid ethanol conversion is seen respectively. Therefore, optimising the operation parameters such as medium pH, liquid and gas flow rates as well as the mass transfer rate between the liquid and the gas phases leads a balanced process [47]. All bacteria need carbon, nitrogen, phosphorous and sulphur as source of energy to grow as well as to synthesize cell materials for their growth [12]. In the concept of syngas fermentation, medium pH plays a crucial role as fluctuations in the pH interferes with the carbon and electron transfer from the substrate toward the cell mass. However, drops in the pH levels (from 6 to 4.5–5.5) due to the activity of the acetogenic bacteria, is in favour of biofuel production as it shifts the reaction to solventogenesis [3]. Among the operation parameters, low mass transfer rate between the bacteria and substrate is the major challenge and the rate limiting step of the syngas fermentation due to the low solubility of the syngas components particularly H_2 and CO.

Fermentation of syngas components is a heterogenous process consisting of solid cells, liquid fermentation media and gaseous substrate. Therefore, the mass transfer mechanism between the gas bubbles and reaction site in cells is a complicated process involving micro scale resistance. The insufficient gas transfer phenomena is commonly controlled with increased mass transfer between the gaseous substrate and the fermentation medium (gas-liquid interface) [38,55–57] however it might as well originate from the low gas diffusion levels within the liquid fermentation media surrounded by the bacteria as well as through the microbial mass to the intracellular active reaction sites [5,58]. To date, increasing the volumetric mass transfer coefficient (k_La) in the gas-liquid interface has received a great attention in the gas utilising bioprocessing [57,59]. To achieve high mass transfer in an energy efficient way, advanced biofilm reactors providing high cell concentrations by preventing bacterial wash out is a promising technology to reduce energy intensity of the process [60]. The biofilm reactors applied to syngas fermentation is discussed in Section 3 along with detailed mass transfer mechanisms of the different configurations.

2.1. Biochemical reactions in syngas fermentation

The microbial metabolism is completed through Wood-Ljungdahl or the reductive acetyl-CoA pathway. In this metabolic pathway autotrophic microbes use C1 compounds (CO and/or CO_2) as the carbon source and H_2 as the energy source as the unicarbonotrophic microbes utilise C1 compounds as their both carbon and energy source to maintain bacterial growth [12]. The metabolic pathway starts with series of reduction reactions for the conversion of CO and H_2 to the main intermediate product (Acetyl-CoA) at the acetogenesis step. Subsequently the final products such as ethanol, butanol, acetic acid, acetate and butyrate are produced in the solventogenesis step. The microbial reaction mechanisms are outlined in Fig. 2.

CO can enter the pathway either directly with the Carbonyl (Western) branch or in oxidised form of CO_2 in the reversible water-shift reactions [62]. Produced CO_2 can enter the pathway via Methyl (Eastern) branch depending on the limited availability of the atomic hydrogen as an energy source produced by hydrogenase reaction [3,12]. In Methyl branch CO_2 undergoes sequential, enzyme-catalysed reduction reactions (Fig. 2a) to form a methyl group which reacts with CO sourcing from both direct entry and reduction of CO_2 to form the main intermediate product (Acetyl-CoA) of the. An extremely low reduction potential of ferredoxin (<-500 mV), as an electron donor, is required for the biochemical activity of CO dehydrogenase/Acetyl-CoA synthase enzyme for Acetyl-CoA production [63–65]. As such electron transfer mediators and redox balance determines the efficiency of Acetyl-CoA production and eventually the syngas fermentation yield [66]. The microbial pathway of the CO_2 fixation in the Methyl branch reactions is explained in detail by Ragsdale [67]. In the solventogenesis step (Fig. 2b), Acetyl-CoA is utilised directly in the enzymatic reactions to produce acetate and acetic acid or to produce butanol and butyrate in series of reduction reactions after being converted to Butyryl-CoA [30,68]. On the other hand, metabolite production in Wood-Ljungdahl pathway is widely considered to be controlled thermodynamically [69]. For instance, operation within the mesophilic range was recently reported to be more favourable for production of alcohols and fatty acids than the thermophilic range [46,70]. The main reactions occur in the syngas fermentation process are given in Table 1 along with the Gibbs free energies (ΔG°) in standard conditions. All reactions in the syngas fermentation are thermodynamically favourable and occur spontaneously based on the negative ΔG° values [55]. In addition, ΔG° value of ethanol (Eq 2–6), acetate (Eq 10, 11) and butanol (Eq 13) production from CO are lower than those by metabolising CO_2 and H_2 (Eq 1 for ethanol), (Eq 7, 8 for acetate) and (Eq 12 for butanol). As such acetogens gain more energy utilising CO from the thermodynamics standpoint indicating that electron transfer from CO is thermodynamically more favourable than from H_2. Also the hydrogenase reactions can reversibly be inhibited by CO [30]. The thermodynamic driving force on the other hand, can be managed by using mediators like NADPH, NADH with varying redox potential for extracellular electron transfer [71]. The

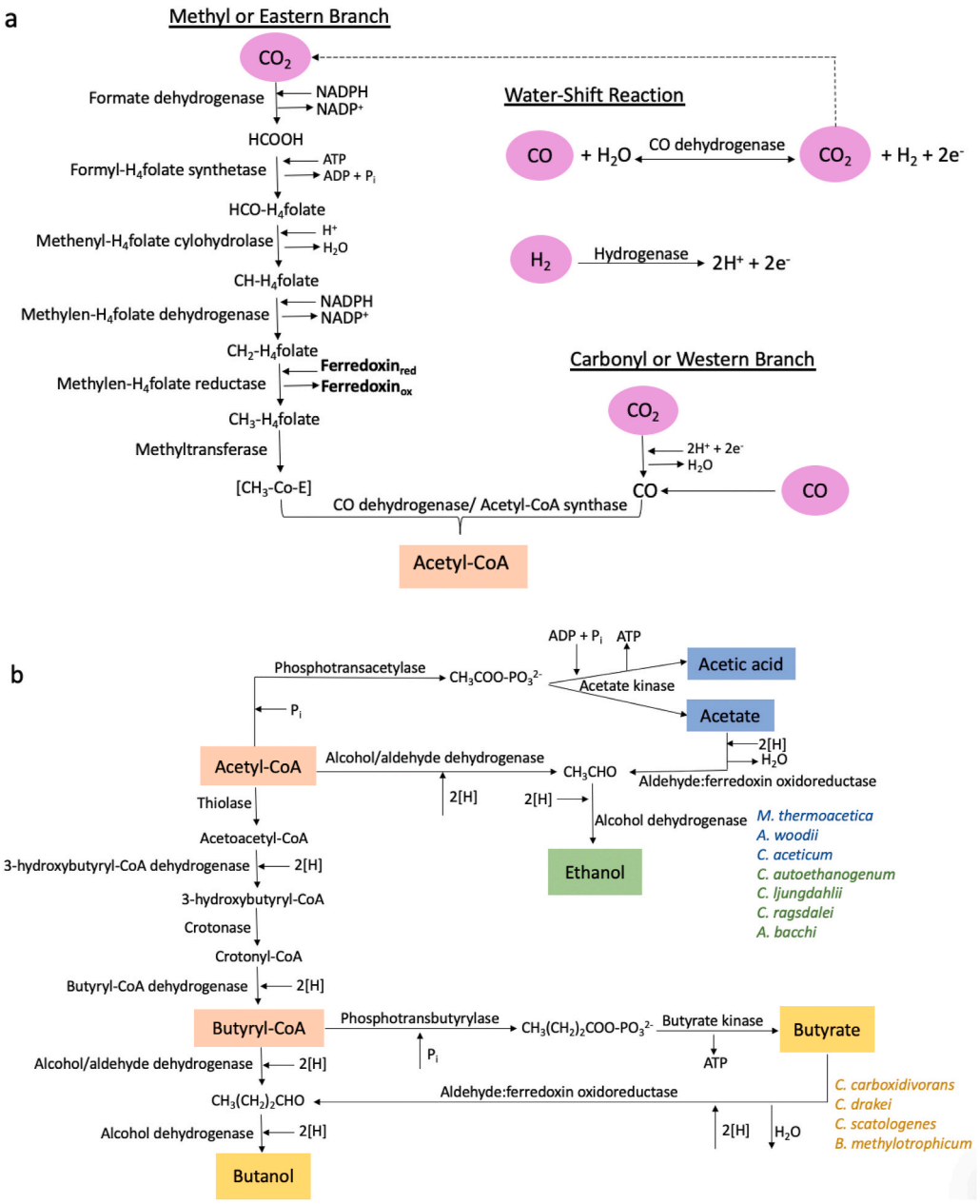

Fig. 2. Wood-Ljungdahl metabolic pathway adopted from Refs. [3,12,30,61] a. Acetogenesis phase, b. Solventogenesis phase. (The common bacteria types involved in solventogenesis phase are colour coded based on the product of interest.).

autotropic bacterial growth where CO is sole source of carbon and energy is reported in detail by Ragsdale [72] with a specific reference to Wood-Ljungdahl pathway.

Biohydrogen can also be produced by syngas fermentation as a result of the reaction between CO present in syngas and H_2O via the biological water shift reaction (WSR) [76]. H_2 production (Eq 20) is thermodynamically much less favourable in comparison with the alcohol and fatty acid production (Eq 1–18). Despite its high energy value, production of H_2 from syngas has received a little attention due the challenges associated with its storage and delivery [77]. Nonetheless, this reaction can potentially be used for enhancing the H_2 content of the syngas by removing generation CO_2, noting that low energy generation leads slow microbial growth an eventually prolongs the operation in steady state.

Biochemical reactions could be inhibited by the accumulation of CO, ethanol and fatty acids. Hydrogen dependent CO_2 reductase acetogens (*acetobacterium woodii*) is particularly known for being sensitive to CO [61]. Therefore, the molar fraction of CO in the feedstock plays an important role when the mix culture is used as biocatalyst in order to maintain the bacterial growth. Accumulation of ethanol and organic fatty acids can potentially inhibit the reaction by breaking the cell integrity. For instance, the accumulation of ethanol might potentially lead hyperpolarisation of the lipid bilayer within the cell membrane. Continuous selective ethanol recovery not only increase bacterial activity, it also increases forward reaction rate from equilibrium standpoint [67,78]. Furthermore, a risk of reaction shift to methanogenesis is also associated with presence of CO in the syngas where the mix culture is used as inoculum source. In order to prevent occurrence of the side reactions due to the bacterial competition and maximise the process yield, bromoethane sulfonate is commonly used to inhibit methanogenesis [46,67]. Accumulation of fatty acids, especially operation at acidic pH, on the other hand, results in intracellular diffusion and potentially interference with proton motive force. As a result of that, microbes spend energy on transporting these metabolites instead of maintaining bacterial growth [70].

Table 1
Common reactions in syngas fermentation process with Gibbs free energy adopted from [46,48,55,73–75].

Product	Biochemical Reaction	Eq.	ΔG° (kJ/mol)
Ethanol	$6H_2 + 2CO_2 \rightarrow C_2H_5OH + 3H_2O$	(1)	−96.0
	$6CO + 3H_2O \rightarrow C_2H_5OH + 4CO_2$	(2)	−220.6
	$5CO + H_2 + 2H_2O \rightarrow C_2H_5OH + 3CO_2$	(3)	−197.3
	$4CO + 2H_2 + H_2O \rightarrow C_2H_5OH + 2CO_2$	(4)	−177.3
	$3CO + 3H_2 \rightarrow C_2H_5OH + CO_2$	(5)	−157.2
	$2CO + 4H_2 \rightarrow C_2H_5OH + H_2O$	(6)	−137.1
Acetate	$4H_2 + 2CO_2 \rightarrow C_2H_3O_2^- + H^+ + 2H_2O$	(7)	−74.4
	$4H_2 + 2CO_2 \rightarrow C_2H_3O_2^- + H^+ + 4H_2O$	(8)	−87.8
	$4H_2 + 2HCO_3^- + H^+ \rightarrow C_2H_3O_2^- + 4H_2O$	(9)	−114.5
		(10)	−172.2
	$4CO + 2H_2O \rightarrow C_2H_3O_2^- + H^+ + 3CO_2$	(11)	−157.5
	$4CO + 2H_2O \rightarrow C_2H_3O_2^- + H^+ + 2CO_2$		
Butanol	$12H_2 + 4CO_2 \rightarrow C_4H_9OH + 7H_2O$	(12)	−486
	$12CO + 5H_2O \rightarrow C_4H_9OH + 8CO_2$	(13)	−245
Acetic acid	$2CO_2 + 4H_2 \rightarrow CH_3COO^- + H^+ + 2H_2O$	(14)	−95.0
Butyrate	$C_2H_3O_2^- + C_2H_5OH \rightarrow C_4H_7O_2^- + H_2O$	(15)	−38.5
	$C_2H_3O_2^- + 6H_2 + 2CO_2 \rightarrow C_4H_7O_2^- + H_2O$	(16)	−143.0
Caproate	$C_2H_3O_2^- + 2C_2H_5OH \rightarrow C_6H_{11}O_2^- + 2H_2O$	(17)	−81.5
	$C_4H_7O_2^- + 2C_2H_5OH \rightarrow C_6H_{11}O_2^- + H_2O$	(18)	−43.0
Water shift reaction	$CO + H_2O \rightarrow CO_2 + H_2$	(19)	−20.1

3. Biofilm reactor configurations applied to syngas fermentation

A variety of biofilm reactors have been used for syngas fermentation at different scales (Table 2). In the following sections, the operational principles of bioreactor configurations used for syngas fermentation was critically reviewed with a particular emphasis on influence of different biofilm technologies on gas-liquid mass transfer (GLMT) rates. Advantages and disadvantages of all reactor types were stated with regards to conventional reactors.

3.1. Trickle bed reactor (TBR)

TBRs are the one of the classical examples of multiphase fixed bed reactors commercialised in 1950s for petroleum industry [82]. In a TBR, bacterial cells are attached on packing material filled in a long column (Fig. 3) as opposed to being suspended in the liquid phase of the slurry reactors [81]. The gaseous substrate and the liquid medium can be fed into to the reactor counter-currently or co-currently in addition to cycling operation where a continuous flow of fluid phase is forced to toggle periodically at the inlet and the outlet of the reactor [83]. The non-linear hydrodynamic nature of the cyclic operation mode over-complicates the process stability and control at full scale implementations therefore counter-current and co-current operations are most preferred [83].

Success of the TBRs is highly dependent on the homogeneous distribution of the fluid phase trickling down the packing where the cells are highly concentrated. Formation of a thin fluid films around packing

Table 2
Studies of syngas fermentation with biofilm technology.

Inoculum	Feed Gas (v/v, %)	Reactor Configuration, Operation mode	Temp. (°C)	Pressure (psi)	pH	HRT (h)	k_La (h^{-1})	Product(s) (g/L)	Conversion Yield (%)	Ref.
Clostridium carboxidivorans P7	$CO/H_2/CO_2/N_2$ (20/5/15/60)	RPBR, 3.3 L, [a]Continuous	37	16.7	4.5–5.5	4	k_La_{CO}: 70	Ethanol: 7.0	Ethanol:[b]0.15 Acetate:[c]0.06	[39]
Clostridium carboxidivorans P7	$CO/H_2/CO_2/N_2$ (20/5/15/60)	MBR, 8 L, [a]Continuous	37	15	4.5–5.5	N/A	k_La_{CO}: 450	Ethanol: 4.89 Acetate: 3.05	X_{CO}: 84.9% X_{H2}: 90%	[79]
Mixed culture	H_2/CO_2 (60/40)	HFMBR, 320 ml, [d]Continuous	55	N/A	6	24	N/A	Acetate: 42.4	N/A	[73]
Mixed culture	CO/H_2 (40/60)	HFMBR, 390 ml Batch	35	1.5–2.2	6	[e]165	N/A	Acetate: 4.22 Butyrate: 1.35 Caproate: 0.88 Caprylate: 0.52	X_{CO}: > 95% X_{H2}: >95%	[46]
Mixed culture	CO/H_2 (40/60)	HFMBR, 390 ml, Continuous	55	1.5–2.2	6	36	N/A	Acetate 27.90	X_{CO}: > 95% X_{H2}: >95%	[46]
Mixed Culture	CO/H_2 (60/40)	HFMR, 320 ml, [a]Continuous	35	5.9–16.9	4.5	9	N/A	Ethanol: 16.9 Acetate: 7.4	N/A	[74]
Mixed culture	H_2/CO_2 (60/40)	HFMR, 320 ml, Batch	35	14.5	4.5–4.8	[e]26	N/A	Acetate: 12.5	X_{H2}: 100% X_{CO2}: N/A	[75]
Mixed culture	H_2/CO_2 (60/40)	HFMR, 320 ml, Continuous	35	14.5	4.5–4.8	72–216	N/A	Acetate 3.6 Butyrate < 0.1	X_{H2}: 100% X_{CO2}: N/A	[75]
Mixed Culture	H_2/CO_2 (60/40)	HFMR, 240 ml	35	5.9	6.0	N/A	N/A	Acetate: 7.4, Butyrate: 1.8, Caproate: 0.98 Caprylate: 0.42	X_{H2}: 100% X_{CO2}: N/A	[48]
Clostridium carboxidivorans P7	$CO/H_2/CO_2/N_2$ (20/5/15/60)	HFMR, [a]Continuous	37	15	4.5–5.5	N/A	k_La_{CO}:1096.2	Ethanol: 23.93 Acetic acid: 4.99	X_{CO}: 53.6% X_{H2}: 68.2%	[34]
Mixed Culture	H_2/CO_2 (60:40)	HFMR, 240 ml, Continuous	35	5.9	6.0	[f]0.25–8	N/A	Acetate: 28.5 Butyrate: 6.3 Caproate: 3.5	X_{H2}: 100%	[80]
Clostridium ragsdalei	$CO/CO_2/H_2/N_2$ (38/28.5/28.5/5)	TBR, 500 ml, Semi Continuous	37	35	4.6–5.8	69	k_La_{CO}:544 k_La_{H2}:260	Ethanol: 5.7 Acetic acid: 12.3	X_{CO}: 91% X_{H2}: 68%	[81]

[a] Batch operation at pH 6 took place prior to continuous operation to establish biofilm formation.
[b] Unit is in mol CO/mol ethanol.
[c] Unit is in mol CO/mol acetate.
[d] 2 batch operations took place prior to continuous operation. Batch 1 – inhibition of methanogenesis, Batch 2 – culture acclimatisation.
[e] HRT is the entire reaction duration (Batch mode), unit in day.

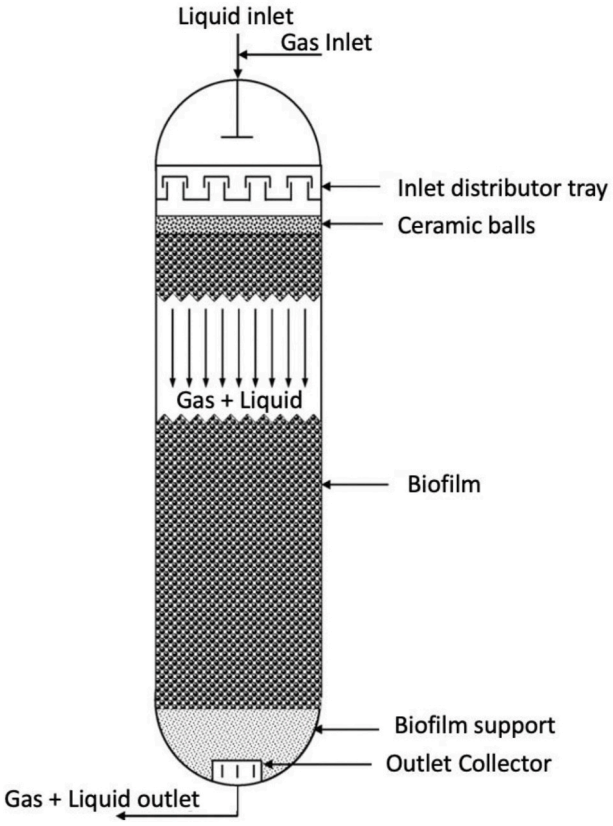

Fig. 3. Schematic diagram of TBR adopted from [84].

reduces the resistance in the GLMT [84]. Achieving high fluid dynamic (close to plug flow regime), operation and maintenance simplicity, ability to operate at elevated pressure and enhancing the mass transfer in the gas liquid interface are the main advantageous of the TRBs in syngas fermentation applications. The major drawbacks, on the other hand, are known to be limitations in medium choice (low viscosity and anti-foaming liquid is essential), maldistribution and/or channelling of the medium on the packing, inhibitory effects of the gas accumulation on the microbes and risk of flooding [84]. These drawbacks can be mitigated by optimising the operation parameters particularly the gas and liquid flowrates. Syngas fermentation applications of the TBRs has received a scant attention in the literature although it significantly increased the k_La value for CO and H_2 in comparison to the conventional reactors and showed in 5.7 and 12.3 g/L ethanol and acetic acid production as a result of 91 and 68% CO and H_2 conversion yields (Table 2) respectively [81].

3.2. Rotating packed bed biofilm reactor (RPBR)

RPBRs developed in 1990s are one of common examples of fixed bed reactors which bacterial immobilisation occurs on cage-like enclosures within the reactor [85]. The horizontally rotating cage is specifically located to be exposed to both the fermentation medium and the headspace (Fig. 4) allowing cells to absorb gaseous substrate from liquid and gas phases alternately [39]. In the liquid phase, mass transfer of the gas molecules from the gas bulk to cell surface includes following stages (1) diffusion to gas-liquid interface, (2) across the interface, (3) diffusion to the liquid bulk and (4) to the cell surface. Direct microbial contact with the gas in the headspace is the distinctive feature for RPBRs which accelerates the mass transfer as the diffusion across the gas liquid interface is the major rate limiting step [45,57,86–88]. It should be noted that microbes attached to the biofilm are covered with the liquid medium in form of a thin film which still generates mass transfer resistance but it is

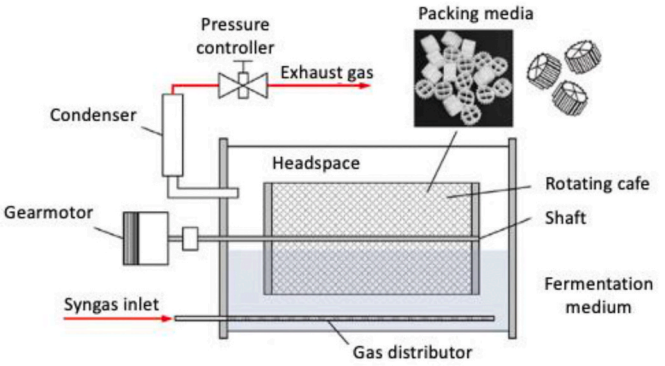

Fig. 4. Schematic diagram of RPBR adopted from [39].

significantly less than the liquid bulk resistance [45]. To conclude, the headspace provides a short cut of mass transfer pathway by eliminating some of the steps stated above [39]. The biofilm formation mechanism particularly in moving bed reactors is reported by Ref. [89].

The rotational speed of the RPBRs is very low (around 5 rpm) rendering the full-scale operations economically feasible. Furthermore, RPBRs outperforms the primitive fixed bed reactors i.e. TBRs in terms of enabling the operation in a wide range of gas, liquid flowrates as well as elevated pressure [84,90]. The main drawbacks of the RPBRs are reported to be risk of pipe clogging and corrosion [85]. Despite its unique mass transfer feature, RPBRs received a scant attention in syngas fermentation concept. The only published study showed a 3.3 fold increase in the ethanol productivity reaching 7.0 g/L yield (Table 2) in comparison to CSTR [39].

3.3. Monolithic biofilm reactor (MBR)

MBR is invented by incorporating monolithic packing materials with bubble column reactors in order to prevent the microbial cell washout during continuous operation as well as to provide a higher cell density with a greater gas-liquid mass transfer (GLMT) efficiency in 1980s [91]. Therefore it is considered to be upgraded version of the bubble column

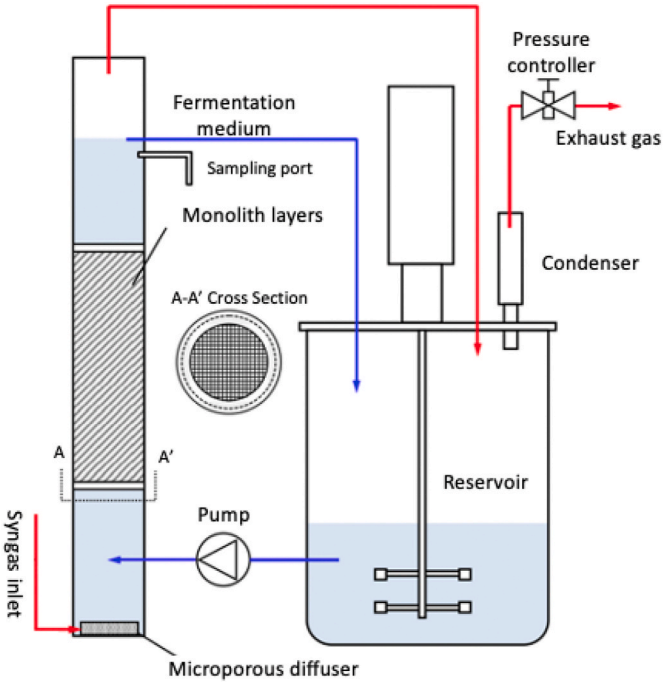

Fig. 5. Schematic diagram of MBR adopted from [79].

reactors [44]. Monoliths are composed of bundle of uniformly structured straight, parallel channels (Fig. 5) with a typical hydraulic diameter of 1–5 mm separated by thin walls [92]. MBR outperforms primitive biofilm reactors such as TBR in terms of maintaining stable pressure throughout the reactor due to presence of minimised bend and physical obstacles owing to its flat structure. The flow characteristics of the MBR was initially reported by Ref. [91] in detail.

Monoliths are considered to be economically feasible packing materials for microbial immobilisation which bring along the advantageous of an increased active surface area as well as a greater mechanical stability [93]. The major operational drawback of the MBR is the risk of channel clogging. MBRs are therefore inflexible in terms of operation parameters such as substrate concentration, liquid and gas flow rates depending on the channel diameter [93].

Although MBR has been widely investigated for multiphase reactions like hydrogenation and oxidation industry [94], it has received a scant attention in the literature for syngas fermentation applications. In the only published study, ethanol productivity enhanced by 53% with regards to bubble column reactor which was operated under the identical conditions. The greater yield is achieved by MBR as a result of increased k_La value for CO (450 day^{-1}, Table 2) and enhanced CO conversion yield (84.9%) [79].

3.4. Hollow-fibre membrane biofilm reactor (HFMBR)

The HFMBRs are well accepted and commonly used for wastewater treatment [95] as well as biofuel generation at varying scales [96]. Similarly, it is the most studied biofilm reactor configuration for syngas fermentation; seven different examples are presented in Table 2.

The HFMBR integrates a membrane filtration into a bubble column reactor (Fig. 6) where the substrate is directly fed through the biofilm supporting gas permeable membrane. The microorganisms naturally attach on the surface of the membrane and proliferate due to supplied nutrients in the medium. End products like ethanol, short or medium chain fatty acids are then diffuse to the bulk liquid to be collected [80].

HFMBR are particularly capable of enhancing the mass transfer rate between the gas and the liquid phases due to large specific exchange surface area of gas permeable membrane [48] and its counter diffusion design [97]. Furthermore, HFMBR allows removal and/or recirculation of liquid and gaseous phases while retaining the solid phase maintaining high cell concentration during operation which renders microbial resilience to potential environmental changes particularly CO toxicity [48,73,75] as well as shortening the required HRTs [95]. Smaller

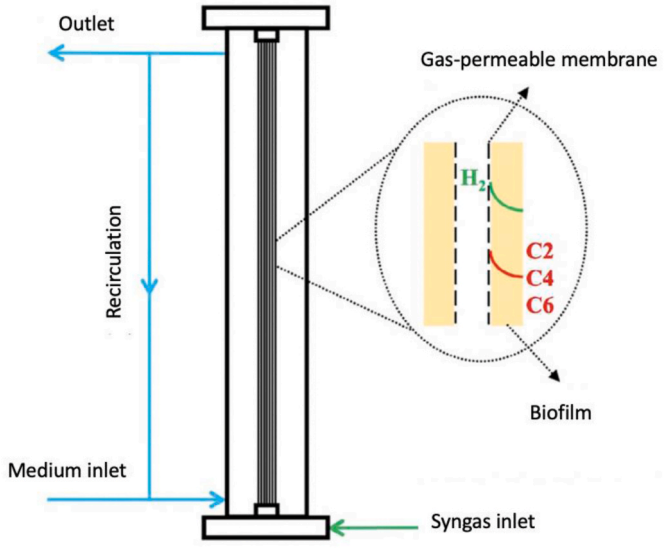

Fig. 6. Schematic diagram of HFMBR adopted from [80].

footprint requirement and lower energy consumption are other important advantageous of the HFMBRs [48]. Despite these advantages, HFMBR has shortcomings such as membrane fouling, concentration polarisation and high capital costs. To date, mass transfer in the gas-liquid interface of the HFMBRs, which is the major bottleneck of syngas fermentation, has received a scant attention despite the broad investigation of the gas conversion yields (Table 2) [46,48,75,80]. Nonetheless, an enhanced k_La value for CO was reported as 1096 h^{-1} by Ref. [34].

4. Strategies for further enhancements of syngas fermentation yields

The economic feasibility of the syngas fermentation for industrial implementation is directly linked to the GLMT as it is the rate limiting step of the process [56,98]. Implementation of biofilm technology is proven to enhance the syngas fermentation yield which brings attention on reactor engineering approach. For instance, incorporating the nanoparticles with the conventional reactors i.e., bubble column reactor creates high cell density by immobilising the bacteria. As a result, the reactor is considered to be upgraded. Biofilm-based reactor configurations owing to the ability of preventing the bacterial cell leakage is an economically feasible [99]. Deployment of the nanoparticles into gas-liquid interface can enhances the mass transfer coefficient by three mechanisms: (i) shuttling or grazing impact, (ii) hydrodynamic interaction at the gas-liquid boundary and (iii) alternations in the gas-liquid specific interfacial area [100,101]. A recent study has proven the enhancement of the fermentation yields when methyl-functionalized cobalt ferrite–silica ($CoFe_2O_4$@SiO_2–CH_3) nanoparticles were used by reporting a 213.5% and 59.6% increase in ethanol and acetic acid production respectively in comparison to the yield of the convectional reactor. The same study also investigated the recovery of the nanoparticles by using a magnet and revealed the reusability up to 5 times without a significant loss in the yields is possible [102]. Similarly addition of activated carbon into fermentation medium increased CO and H_2 solubility correspondingly the ethanol productivity rose from 1 g/L to 19 g/L [3]. In addition, it is known that operation of syngas fermentation at elevated pressure increases gas solubility according to Henry's law which correspondingly increases the mass the GLMT rates. The influence mechanisms of the high partial gas pressure on the production yield is reported in detail by Ref. [103]. Moderately high pressure syngas fermentation operation, upon to 4–5 bar (58–72 psi), is reported to be economically feasible [104,105]. Several studies integrated the high-pressure operations to varying biofilm reactor configuration with a maximum pressure level of 35 psi (Table 2). As a result, increased product yields were achieved, based on increased k_La values. Along with achieving increased gas solubility in the liquid medium, GLMT rates and specific surface area for bacterial activity, oxidoreductases play an important role in enhancing the syngas fermentation yield as they control the biochemical reactions of the metabolic pathway. Hence, both electron transfer and redox balance are also crucial parameters to be taken into account in order to achieve enhanced syngas fermentation kinetics and yields biofilm reactor configurations [66]. As such development of electro-fermenters by incorporating electrochemistry into single and mixed culture fermentation processes is a promising technology in terms of achieving a greater product selectivity and carbon conversion efficiency while limiting the use of redox balancing and pH control additives [106,107]. In a typical electro-fermenter, supplementary electron source or sink is provided by a closed circuit achieved by connecting two electrodes and the robustness of the process depends on (i) microbial interactions while forming biofilm, (ii) dissolved redox mediators present in the medium, (iii) interactions between bacteria and the electrode surface through transfer of electrons extracellularly [108]. The redox mediators like NADH and NADPH (Fig. 2) acts as electron shuttles in extracellular electron transfer mechanism allowing microbes proceeding with electrocatalysis by

coupling intracellular metabolism with extracellular substrate redox [109]. In such systems however, balancing redox mechanisms between acetogenesis and solventogenesis phases is required for successful operations [66]. Another strategy for achieving further enhancements in the syngas fermentation is combining biofilm technology with increased end product selectivity by bacterial genome modification [6,110].

5. Industrial implications of syngas fermentation

In spite of many research activities conducted from lab to pilot scale at various universities and institutes, so far only three companies have reported the successful full-scale syngas fermentation operations [30, 111].

The first gas-to-ethanol facility, known as Coskata Inc. Was founded in 2006 in USA and operated at a capacity of 23.7 kt/year for approximately for 2 years starting from 2009 [112]. As, Coskata Inc. transferred to syngas fermentation from methane reforming background, both biomass resource and natural gas is used as feedstock at the site. In 2015 Coskata Inc. formed the basis of Synata Bio which then diverted to valuable chemical like acetic acid, propanol and n-butanol in addition to ethanol [113,114]. Following Coskata Inc., INEOS Bio was established in USA in 2003. INEOS Bio is known to be a pioneer in the second-generation fuels as the company was first to combine gasification with syngas fermentation for ethanol production in order to utilise the lignocellulosic compounds fully [115]. In 2011, INEOS Bio constructed its first semi commercial plant in cooperation with New Plant Energy for production of bioethanol from municipal and agricultural wastes. The plant stayed in operation by late 2014 with a capacity of 23.7 kt/year in addition to 6 MW electricity production [38]. However, INEOS Bio and Coskata stopped operation due to the operational and financial difficulties [3].

LanzaTech launched in New Zealand in 2005 at a pilot scale to process syngas and CO rich industrial exhaust gas for ethanol and 2,3-butanediol production [30]. By 2012, LanzaTech started operation at full scale and, in collaboration with Chinese steel industry, became the biggest company in the field with an annual ethanol production capacity of 300 Mt. Furthermore, LanzaTech is currently developing 3 syngas fermentation plants to go into operation in Belgium, China and Swayana with an annual ethanol production capacity of 62 000, 48 000 and 52 000 Mt respectively. In addition, Genomatica and Kiverdi are also in the process of commercialisation of syngas fermentation [3]. Due to the company confidentiality, detailed reactor configuration and the operation conditions of the plants are not available in literature. However, patent specifications indicated the use of CSTR and loop reactors for INEOS Bio and LanzaTech respectively [38]. Furthermore, continuous operation of bubble column reactor was reported to be the configuration of the planned LanzaTech plant in Belgium [104].

Although, the adoption of biofilm reactors has shown a greater gas conversion yields, GLMT rates as well as process stability based on the research conducted since the last decade (Table 2), it has not been transferred to the full-scale applications yet. The major limiting factors in the technology transfer is known to be (i) limited reusability of the cultures under continuous operation mood, (ii) potential diffusion resistance to the feedstock and the nutrients arising from excessive biofilm thickness, (iii) potential reactor blockage risk in long term use depending on the biofilm porosity [116], (iv) limitations in diffusion of extracellular product into the medium, (v) long bacterial immobilisation time at the start-up phase, (vi) challenges in scaling up of the biofilm supporting materials [43] and (vii) challenges in the control of the uniform biofilm formation [117]. Therefore, industrial applications of the biofilm processes are required a comprehensive optimisation and feasibility study. Nonetheless, the first commercialisation attempts of biofilm reactors were already taken place. In this regard, several patent examples were seen for TBR (Section 3.1) [118], HFMR (Section 3.4) [119,120] and moving bed reactors i.e RPBR (Section 3.2) [121] as the first step of the technology transfer.

6. Research gaps and future prospects

Although the biofilm catalysed syngas fermentation (coupled with gasification of lignocellulosic biomass or with industrial exhaust gas) is a promising technology for biofuel and value-added chemical production, there are some challenges in scaling up to industrial applications. The biggest challenge is considered to be commonly applied empirical methodologies in the fundamental syngas fermentation. Furthermore, to date developing novel biofilm reactors has received a very scant attention in the literature. The major research gap was identified as the non-existing link between applicability of this technology at micro and macro scales with regard to testing process stability. Incorporating computer simulation tools into empirical experiments can facilitate the progressive scale up processes by enabling a rapid investigation of many different scenarios with accurate yield predictions. Given that the diffusion of media inside the biofilms is also a major obstacle, the future research on biofilm reactor configurations should focus on the (i) design of novel packing materials to shorten the biofilm formation time, (ii) development of inexpensive medium and biofilm support components, (iii) optimisation of biofilm thickness to prevent the resistance in diffusion of media inside of the biofilms, (iv) assessment of optimum biofilm dispersion by cost effective synthetic biology approaches for an enhanced biocatalysts capacity, (v) design of novel bioreactors to further enhance GLMT and productivity while minimising energy consumption during operation as well as (vi) completion of a techno economic assessment and the scale-up potential with a technology integrated experimental approach in order to render this technology transferable to industrial scale cost effectively.

7. Conclusions

As outlined in this review, the global energy demand is increasing enormously therefore a thriving research effort went initially into the investigation of the 2nd generation renewable biofuels. Biofuels generated via biochemical conversion of syngas can provide an efficient solution to the energy scarcity issues while contributing to the climate change mitigation strategies of the EU. The greater potential of biofilm-based catalysis in comparison to the conventional metal catalysis to convert exhaust gas and/or gasified lignocellulosic biomass substrates into the environmentally friendly biofuels and value-added chemicals has been confirmed by the literature as a sustainable energy management method. The state of art findings reinforce the necessity of the widespread adoption of the biofilm-based catalysis for syngas conversion due to its capability of achieving a greater process stability, intensity and flexibility with a minimal operational expenditures. In spite of its inherit merits, no examples of biofilm catalysis at commercial scale were seen so far. A significant further research effort should be made toward minimalisation of the biofilm formation time and optimisation of the biofilm thickness to prevent diffusion resistance as well as their techno-economic evaluations for achieving cost effective and reliable full-scale applications.

Declaration of competing interest

The author declares no interest.

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