

## A review of biomass-derived fuel processors for fuel cell systems

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### ABSTRACT

Fuel cell coupled with biomass-derived fuel processor can convert renewable energy into a useful form in an environmental-friendly and CO<sub>2</sub>-neutral manner. It is considered as one of the most promising energy supply systems in the future. Biomass-derived fuels, such as ethanol, methanol, biodiesel, glycerol, and biogas, can be fed to a fuel processor as a raw fuel for reforming by autothermal reforming, steam reforming, partial oxidation, or other reforming methods. Catalysts play an important role in the fuel processor to convert biomass fuels with high hydrogen selectivity. The processor configuration is another crucial factor determining the application and the performance of a biomass fuel processing system. The newly developed monolithic reactor, micro-reactor, and internal reforming technologies have demonstrated that they are robust in converting a wide range of biomass fuels with high efficiency. This paper provides a review of the biomass-derived fuel processing technologies from various perspectives including the feedstock, reforming mechanisms, catalysts, and processor configurations. The research challenges and future development of biomass fuel processor are also discussed.

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## 1. Introduction

In response to the escalating energy crisis and related pollution problems, we urgently need to adopt new energy supply technologies that utilize renewable energy sources in an efficient and environmentally friendly manner. Fuel cell has been identified as one of the most promising technologies for the future clean energy industry [1]. It converts the energy chemically stored in a fuel, such as hydrogen, into an electrical energy output by electrochemical reactions. The fuel cell operation is efficient, clean, and silent. Fuel cell can be applied to large-scale stationary systems for distributed power generation as well as small-scale portable power supply devices for micro-electronic equipment and auxiliary power units (APU) in vehicles [2].

Presently, hydrogen is commonly used as a fuel to energize fuel cells, especially for proton exchange membrane fuel cells (PEMFCs). If a raw fuel, such as diesel, natural gas, and methanol, is used, a fuel processor is needed to reform it into a hydrogen rich gas for the fuel cell to perform the electrochemical conversion in the fuel cell system [3].

Fuel cell can also work with biomass for renewable electricity supply. Recently, the biomass-derived fuel has received a lot of research interests due to its innate advantages over conventional fossil fuels. Biomass is renewable, clean, carbon neutral, and widely available. Many research works have been done on hydrogen production from biomass by various methods, such as gasification and fermentation (Fig. 1). However, most of these methods are not specially designed for fuel cells; thus, they can only partially meet the specified requirements of fuel cell application in terms of output energy density, hydrogen yield, product gas purity, start-up time, emission, as well as equipment size and weight, especially for portable and on-board applications.

It is important to understand the past and ongoing technological development in order to further develop the promising biomass-derived fuel processor for fuel cell systems. This paper overviews the relevant research on biomass and the fuel cell, with an emphasis on the experimental studies.

## 2. Biomass-derived fuel types

Many literatures have reported direct utilization of solid biomass, such as wood and straw, to produce hydrogen by pyrolysis and gasification. These methods are highly regional dependent. Comparatively, biomass-derived fuels, which are produced from biomass, appear to be more suitable for fuel cells in both stationary and portable applications because most of the biomass-derived fuels in either liquid or gas form are easy to transport and the infrastructures needed are readily available. Moreover, the production and utilization of biomass-derived fuels are much more technologically ready. Thus, the two-step utilization (biomass → biomass-derived fuels → hydrogen) is more favorable before the technologies of hydrogen storage and transportation are mature enough for cost-effective industrial use. In the following sections, different kinds of biomass-derived fuels for the fuel cell application are reviewed. Some of them have already been widely used while others have a great promise for future development.

### 2.1. Bio-ethanol and bio-methanol

Bio-ethanol and bio-methanol are ethanol and methanol, respectively, produced from biomass. They are promising renewable fuels for fuel cells as they have a hydrogen content. They are also widely available.

The technologies of bio-ethanol production are more mature than that of bio-methanol. Traditionally, it is produced by fermentation of biomass sources, varying from agriculture energy plants to organic wastes. The lignocellulosic residues of cereals have received increasing interests recently in the feedstock of bio-ethanol because it could lower the production cost as well as the risk of food insecurity [4]. However, removal of crop residues may cause soil degradation. Thus, identifying alternative sources of bio-ethanol feedstock is of a high priority. Recent research reveals that animal manure waste, municipal solid waste, waste paper, and citrus peel waste can be the feedstock of bio-ethanol by saccharification and fermentation [5–7].

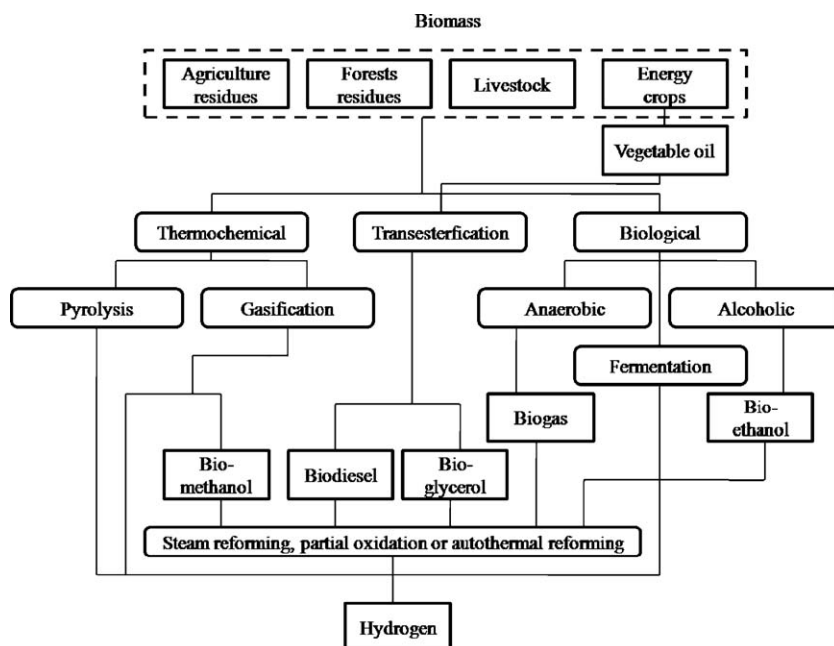


Fig. 1. Selected hydrogen production technologies from various biomass.

Currently more than 75% of methanol is produced from natural gas and coal which are non-renewable. Alternatively, renewable methanol could be produced from biomass, such as wood and agricultural waste, by steam gasification, pyrolysis, or partial oxidation [8]. Presently, renewable methanol is not popular because of the high cost of production. Efforts have been made to lower the cost. Nishigami et al. [9] proposed a method for large scaled bio-methanol production from wood and water using a solar power generation system in the desert. Hirano et al. [10] theoretically investigated the production of bio-methanol by partial oxidation of a microalga, *Spirulina* at 1123–1273 K. The highest theoretical yield is 0.64 g of methanol from 1 g of biomass. Isayama and Saka [11] proposed a two-step supercritical method (Saka–Dadan process) to produce methanol from biomass in a thermochemical process. The method consisted of hydrolysis of triglycerides in subcritical water and subsequent methyl esterification of fatty acids in supercritical methanol treatment. It was found more useful than one-step methanol production method.

The bio-ethanol and bio-methanol have been the most commonly used biomass-derived fuels for fuel cell systems for the past decade and will continue to play an important role in the near future. When comparing the two fuels, ethanol has extra advantages in terms of power density, non-toxicity, storage, transportation, and safety [4]. However, because of incomplete oxidization, the ethanol processing reaction consists of more complicated multistep reaction mechanism and involves a number of adsorbed intermediates and byproducts [12]. It may greatly reduce the output energy density. Moreover, the reaction kinetics of ethanol on catalyst surface is poorer than that of methanol. However, ethanol as a feedstock of fuel cell is still competitive to methanol due to the advantages mentioned above. The deactivation of the reforming catalyst is the major problem of bio-ethanol/methanol reforming due to possible carbon deposition during the ethanol/methanol decomposition, particularly at a high temperature [13]. The side-reaction could also decrease the fuel cell performance.

## 2.2. Biodiesel

Biodiesel is produced from vegetable oils and is therefore a renewable fuel. It is non-toxic and biodegradable. Biodiesel is usually derived from the transesterification of vegetable oil with methanol or ethanol. During the production process, the oil is mixed with a metallic base (e.g. sodium or potassium hydroxide) and an alcohol (e.g. methanol or ethanol). The reaction produces methyl or ethyl ester (biodiesel) and glycerol as a byproduct [14]. The glycerol can also be used as a biomass raw fuel or materials as discussed in Section 2.3.

For the past decade, biodiesel has been gaining worldwide popularity and research interest in utilization in vehicle engines and other kinds of internal combustion (IC) engines as an alternative energy source to petro-diesel [15]. It should be noted that biodiesel is also a promising feedstock for fuel cells. Biodiesel has shorter carbon chains than the original oils and thus it is easier to reform to high quality hydrogen rich gas for fuel cell applications [14]. However, this technology is still in the early R&D stage and only a few literatures can be found [14–18].

Reforming of biodiesel to generate hydrogen can occur without catalysts at around 1673 K in a fuel processor. Catalyst can be used to activation the reaction at a lower temperature and to achieve better control of reaction kinetics [15]. Due to the long carbon chain of biodiesel, the catalyst systems will be deactivated by rapid carbon formation. Fuel cell complications were observed during soy-based biodiesel steam reforming, causing a decrease in performance for both PEM fuel cell and processor [16]. In another

study, canola-based biodiesel was converted into hydrogen rich gas by steam reforming. The rapid carbon formation problem also occurred [16]. So far, no report has shown successful reforming of biodiesel with high efficiency and long-term stability. Further work should be conducted to develop catalysts with higher resistibility against deactivation for biodiesel fuel processor-fuel cell systems.

## 2.3. Bio-glycerol

Glycerol is an alcohol which has a high energy density [19–21]. It is non-toxic, non-volatile, and non-flammable. It is usually used for personal care and food production [22,23]. Bio-glycerol is a byproduct of biodiesel production. Theoretically, three moles of bio-glycerol can be produced accompanied by one mole of biodiesel. With rapid growth of biodiesel production, it provides the possibility to use bio-glycerol as a source of producing hydrogen for fuel cells in large-scale application. Most importantly, bio-glycerol can be produced in a renewable, environmental-friendly, and cost-effective manner.

Works have been done on steam reforming of glycerol to produce hydrogen rich gas for fuel cells. Bio-glycerol is expected to have similar characteristics as its alcoholic congeners in the reforming processes. However, poorer performance was observed in the glycerol processing. Previous studies [22,23] indicated that under the same catalyst (such as Ni/Al<sub>2</sub>O<sub>3</sub>), the hydrogen selectivity for glycerol was much less than that for ethanol (<60%) due to the formation of light alkanes under the same operating condition. The problem also occurred when diluted aqueous solution of glycerol was used.

However, if the system is designed properly, acceptable hydrogen selectivity could be achieved. A recent study by Zhang et al. [24] reported the steam reforming of glycerol over Ce supported Ir, Co and Ni catalysts with respect to the nature of the active metals and the reaction pathways. The Ir/CeO<sub>2</sub> catalyst showed quite promising catalytic performance with hydrogen selectivity of more than 85% and 100% glycerol conversion at 673 K.

The autothermal reforming (ATR) of glycerol can also be employed to fuel cells [23]. Catalyst, washcoat, carbon-to-oxygen ratio, and steam-to-carbon ratio are the major factors that affect the H<sub>2</sub> production. Different catalysts and supports can be selected for the ATR of glycerol, such as Pt over Al<sub>2</sub>O<sub>3</sub>, Rh/CeO<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub> washcoat layer, etc. Under the optimal condition, selectivity to minor products, such as acetaldehyde, ethylene and methane, can be controlled below 2% [23].

## 2.4. Biogas

Biogas is a renewable power source and extensively produced today in an indigenous local base by anaerobic biological waste treatment [25]. It mainly contains methane and CO<sub>2</sub>. Table 1 shows the composition of biogas produced from different biological wastes [26].

There are rapidly increasing usage and production of biogas all over the world. For example, as a source of primary energy in Europe, biogas consumption is expected to reach a target of 15 million tons of oil equivalent (TOE) in 2010 [27]. Due to the presence of CO<sub>2</sub>, most of the biogas is used in an inefficient way, such as combustion in IC engine or burning for heat. Its potential use in fuel cells could increase its energy conversion efficiency and reduce its NO<sub>x</sub> emissions to the atmosphere [27].

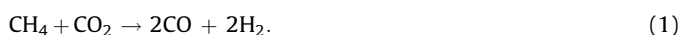
High-temperature fuel cells, such as solid oxide fuel cell (SOFC), are more suitable for the application of biogas [28]. It is because high-temperature fuel cell has a better capability of thermally integrated biogas reforming and more manageable tolerance

**Table 1**  
Compositions of biogas produced from various biological wastes.

Samples	Resource	Composition (%)		
		CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub>
1	Cow manure	60.2	39.8	Not detected
2	Pig manure	66.9	33.1	Not detected
3	Sludge and wet refuse	61.4	38.5	0.14

against fuel contaminants with a high efficiency (30–50%) [28]. Recently, a 100-kW SOFC system fed by biogas has been reported to achieve an electrical efficiency of about 48.7% [29]. Moreover, 1-kW<sub>el</sub> and 5-kW<sub>el</sub> SOFC units (1173 K, 28% and 40% LHV efficiency, respectively) using biogas have been in operation in Switzerland and Canada, respectively, as reported in 2002 [28,30]. References for biogas fed low-temperature fuel cells are also available [31].

Besides steam reforming and partial oxidation, biogas could be reformed by dry reforming [32,33],



The dry reforming takes advantage of the large amount of CO<sub>2</sub> present in biogas as oxidizer in the gas reforming. However, for biogas streams with a CO<sub>2</sub>/CH<sub>4</sub> ratio less than 1, additional alternative oxidizer, such as O<sub>2</sub>, is required. Moreover, dry

reforming could function as part of autothermal reforming together with steam reforming and partial oxidation.

The deposition of carbon on the catalyst is the major problem in dry reforming of biogas and, consequently, the useful life for catalyst is short [34]. Therefore, the use of catalyst in dry reforming of biogas is crucial.

### 2.5. General aspect

There are some other biomass-derived fuels which could be alternatives to the non-renewable fuel as feedstock of fuel cell systems in the near future. Some studies have already been done on reforming of novel biomass-derived fuels (Table 2). The performance and cost of the selected biomass-derived fuels are summarized in Table 3. For comparison, the non-renewable diesel is also included in the table.

From the literature, it can be found that the research works mainly focus on two aspects which are cost and power density. It is important to seek more economical biomass fuel with potential for fuel cell applications. For example, vegetable oil is usually utilized for producing biodiesel for fuel production. However, the cost of one-step utilization (vegetable oil → hydrogen) is expected to be much lower than that of the two-step counterpart (vegetable oil → biodiesel → hydrogen). Therefore, it attracts research interest. Vegetable oil and naphtha have some similar properties.

**Table 2**  
Selected biomass-derived fuels.

Biomass-derived fuels	Resources	Reforming types	Catalysts used	Advantages
Dimethyl ether [35–40]	Dehydration of methanol, or directly gasification from biomass	SR, ATR, Internal reforming	Pt-based; CuFe <sub>2</sub> O <sub>4</sub> ; Cu–Mn; Ce–ZrO <sub>2</sub>	High H/C ratio and energy density; non-corrosive and non-toxic; convenience in handling, storing, and transporting
Glucose [41–46]	Derived from energy crops and fruit juices, etc.	POX, Bio-processing	Submonolayer; silver modified gold film; enzymes	Effective feedstock for biofuel cell as well as normal fuel cell; easy to produce
Ethylene glycol [47–49]	Pyrolysis of biomass	SR, ATR, Internal reforming	Carbon-supported IrSn; Pt, Pt–Au; Ni/olivine, Ni–YSZ;	Safer operation, high energy density, easy to reform
Vegetable oil [50,51]	Derived from energy crops, e.g. rapeseed, sunflower, etc.	SR, Internal reforming	Ni-based; Ce, Ce–Cu, and Ce–Rh	Economical, extraordinary environmentally friendly, easy to collect, abundant yield

**Table 3**  
Comparison of cost of biomass-derived fuels and their performance in reforming process.

Fuel	Formula	Price <sup>a</sup> (US\$/ton)	Reforming performance			References
			Fuel conversion (%)	Hydrogen selectivity (%)	Catalysts and reforming type	
Diesel	C <sub>12</sub> H <sub>26</sub> <sup>b</sup>	766 <sup>c</sup>	96 (12 h)	98	Rh/Al <sub>2</sub> O <sub>3</sub> ; SR	[52]
Bio-methanol	CH <sub>4</sub> O	NA <sup>d</sup>	100 (1000 h)	100	Zn–Cr; POX	[53]
Bio-ethanol	C <sub>2</sub> H <sub>6</sub> O	766 <sup>e</sup>	100	95	Rh/Al <sub>2</sub> O <sub>3</sub> ; SR	[4]
			100	96	Ni/Al <sub>2</sub> O <sub>3</sub> ; SR	[4]
Biodiesel	C <sub>19</sub> H <sub>35</sub> O <sub>2</sub> <sup>b,f</sup>	905	Unsteady	Unknown	SR	[16]
Glycerol	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	1016	80	60	AuPd; SR	[22]
			100	85	Ce/Ir; SR	[24]
Biogas	CH <sub>4</sub> + CO <sub>2</sub>	NA <sup>d</sup>	100	100	Ru/γ-Al <sub>2</sub> O <sub>3</sub> ; ATR	[34]
Dimethyl ether	C <sub>2</sub> H <sub>6</sub> O	557 <sup>g</sup>	100	72	Ce–ZrO <sub>2</sub> ; SR	[40]
			100	51	Ni/Al <sub>2</sub> O <sub>3</sub> ; SR	[40]
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	279	100	unknown	Enzymatic	[45]
Ethylene glycol	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>	1462	84.6	90	Ni/olivine; SR	[48]
Vegetable oil	C <sub>59</sub> H <sub>94</sub> O <sub>5</sub> <sup>b,h</sup>	700 <sup>i</sup>	Unsteady	Unknown	Ni; SR	[50]

<sup>a</sup> The prices were cited from [54,55], which was the average instant prices in P.R. China, on the date of February 19, 2008. Real prices will vary up and down according to different regions and manufacturers. If not explicated, the prices referred to factory prices.

<sup>b</sup> Average formula.

<sup>c</sup> Retail price.

<sup>d</sup> Not commercially available.

<sup>e</sup> Price of ethanol derived from cassava, with concentration of 95%.

<sup>f</sup> Formula of Canola Methyl Ester (CME biodiesel).

<sup>g</sup> Price of dimethyl ether with fuel standard.

<sup>h</sup> Formula of canola oil.

<sup>i</sup> Price of palm oil.

Marquevich et al. [50] successfully reformed sunflower oil with similar commercial nickel-based catalysts and similar process conditions as conventional steam reforming of naphtha. However, it was also reported that carbon formation began after only 14 h of operation. Dupont et al. [51] carried out sunflower oil steam reforming catalyzed by Ni-based catalysts on oxygen transfer material in bench-scale reactors and micro-reactors. The fuel decomposition was also observed in the reforming process which played a significant role in the H<sub>2</sub> production. However, the study found that the coking in the reactor did not gradually lower the system efficiency, because in the steam reforming process, the lay-down carbon will be completely oxidized under the cyclic feedstock.

With the rapid development of micro-fuel cell for portable electronic applications, biomass fuels with high power density become another topical research area. Ethylene glycol could be produced from biomass in a renewable way and it is the main component of bio-oil derived from biomass pyrolysis. Ethylene glycol is safer in operation than methanol and has a theoretical capacity of 4.8 Ah ml<sup>-1</sup>, which is 17% higher than that of methanol [47]. Kechagiopoulos et al. [48] used a novel spouted bed reactor to reform ethylene glycol. The effect of reaction temperature and steam to carbon ratio in the feed was investigated with various catalytic and non-catalytic particles. Coke formation was drastically limited and high hydrogen yield of 80% at 1123 K was achieved when Ni/olivine catalyst was used. The Ni/olivine catalyst is demonstrated as effective to the ethylene glycol reforming, due to the strong Ni–olivine interaction developed during calcinations. Ethylene glycol could also be converted in a direct fuel cell system to release electrons. It is especially suitable for micro-fuel cells [49]. A direct ethylene glycol fuel-cell has been built by Livshits et al. [47]. The fuel cell is based on a nanoporous proton-conducting membrane (NP-PCM), and it proves that ethylene glycol could be a practical fuel.

### 3. Biomass-derived fuel processing system

In a fuel processing system, the most important part is the fuel reformer, which converts the fuels, i.e. biomass-derived fuels, into hydrogen rich gas. The process could be steam reforming, partial oxidation, and autothermal reforming. A vaporizer is always necessary to preheat the fuels, steam, and air before they are fed to the reformer. After the reforming process, CO purification and CO<sub>2</sub> capture steps could follow if necessary. Then, the purified H<sub>2</sub> rich gas will be fed to the fuel cell to generate electricity. For a better design of thermal balance in the whole process, heat recovery devices are always included in the fuel processor–fuel cell systems (Fig. 2). Higher system efficiency can be achieved by combined heat and power generation system (CHP). In a CHP system, the exhaust gas from fuel cell which contains unconverted hydrogen and fuel can be burned in an afterburner to generate additional thermal energy. Thus, both electricity and heat can be produced by the CHP

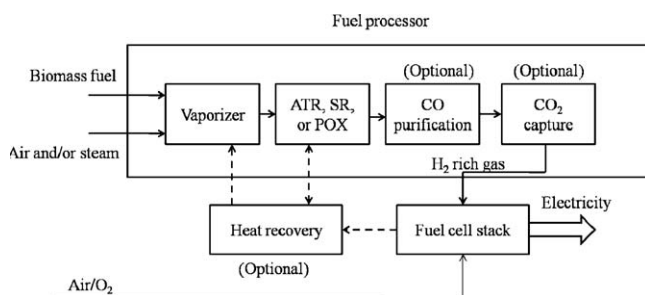
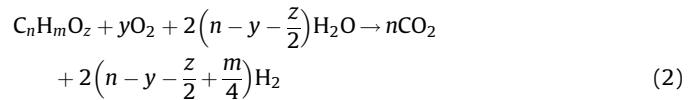


Fig. 2. Fuel processor–fuel cell system.

system. The overall system fuel utilization could exceed 90% [56]. Various designs of fuel processors for better control of mass and thermal conversion are illustrated in Fig. 3.

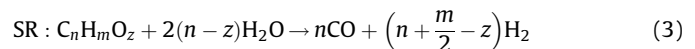
#### 3.1. Reforming process

Different biomass fuels could be considered as the raw fuel for hydrogen production in fuel processor–fuel cell systems. Most of them are hydrocarbon or oxidative hydrocarbon with a general molecular formula of C<sub>n</sub>H<sub>m</sub>O<sub>z</sub>. The overall reforming reaction of hydrocarbons can be written as

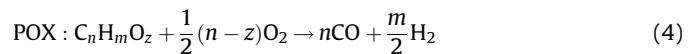


Eq. (2) expresses the ideal reforming reaction in which the H in the hydrocarbons and H<sub>2</sub>O are completely converted into H<sub>2</sub>; the C are completely converted into CO<sub>2</sub>; and neither CO nor any other low-carbon hydrocarbon is formed. To optimize the reforming reaction, the thermodynamics and the performance of the reforming reaction should be analyzed and evaluated. There are three common reforming reactions for the fuel processor: steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR).

SR (Eq. (3)) is quite effective for hydrogen production by separating hydrogen from carbon with the presence of high-temperature steam [57]. But the process is largely endothermic so it will consume a lot of heat. This process has been widely used for the fuel reforming of methane. Low pressure, high temperature, and high steam ratio are favorable conditions for the steam reforming [14].



POX (Eq. (4)) partially burns a fuel stream with a sub-stoichiometric amount of air [14]. The POX approach has advantages of flexibility, which is significant for the APU application that requires short start up time, simple and reliable operation. Additional advantages include good load following characteristics and easy conversion of long-chain hydrocarbon fuels [14]. Regarding the disadvantages of POX, it is more selective to CO than SR and ATR; and it is an exothermic process so the calorific value of the hydrogen rich gas product is lower than that of the original feedstock [57].



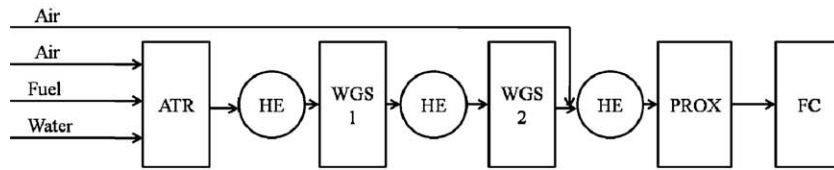
In ATR, the POX and SR take place in one reactor which means the hydrocarbon feed is reacted with both steam and air (oxygen) to produce a hydrogen-rich gas. In order to operate the fuel processor in a steady condition, the ATR must be controlled in a thermally neutral or under slightly exothermic condition [59]. Thus, it is important to study the design parameters of the processor, such as fed oxygen to carbon ratio, hydrogen yield, and efficiency to keep the reaction enthalpy  $\Delta H \leq 0$ . The ATR reaction is more selective to CO<sub>2</sub> than CO [14]. It is widely used in the fuel cell systems for APU.

#### 3.2. CO purification

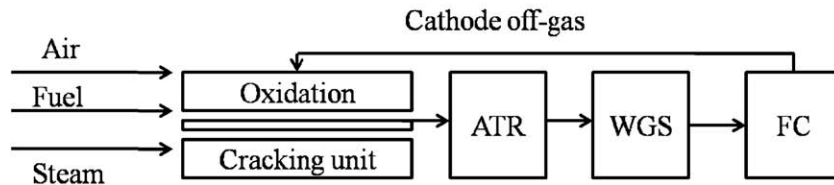
In order to avoid poisoning of the electrocatalyst, low-temperature fuel cell, such as PEMFC, should be fed with CO-free hydrogen. In this case, the fuel processor requires hydrogen purification and CO abatement to reduce the CO level below



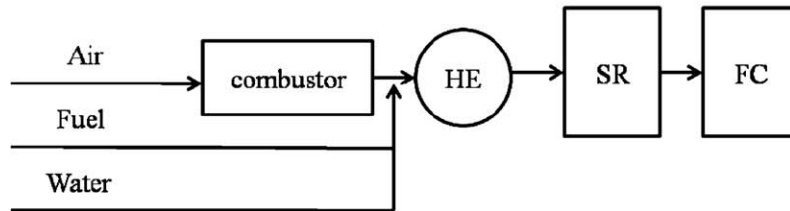
(a) Fuel processor with autothermal reformer, high and low temperature water–gas shift units, PROX unit and heat exchangers [58];



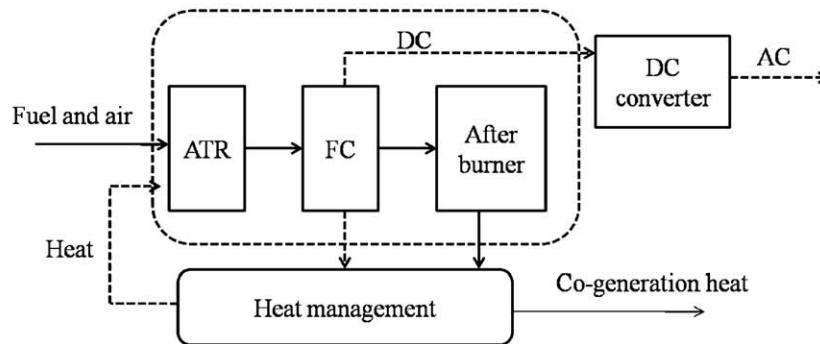
(b) Fuel processor with autothermal reformer, cracking and complete oxidation unit and water–gas shift unit [59];



(c) Fuel processor with combustor and SR reformer;



(d) Fuel processor–fuel cell CHP system.



**Fig. 3.** Various fuel processor designs. (a) Fuel processor with autothermal reformer, high and low temperature water–gas shift units, PROX unit and heat exchangers [58]; (b) fuel processor with autothermal reformer, cracking and complete oxidation unit and water–gas shift unit [59]; (c) fuel processor with combustor and SR reformer; (d) fuel processor–fuel cell CHP system. Note: ATR, autothermal reforming reactor; SR, steam reforming reactor; HE, heat exchanger; WGS, water–gas shift reactor; PROX, CO preferential oxidation reactor; FC, fuel cell.

50 ppm. On the other hand, high-temperature fuel cells, such as SOFC, could use CO as a fuel so that the hydrogen rich gas can be fed to the SOFC directly from fuel processor.

CO abatement always takes place after the primary processing step. During the process, CO is converted with a water steam into CO<sub>2</sub> by exothermic water–gas shift reaction (WGS, Eq. (5)) or oxidized by CO preferential oxidation (PROX, Eq. (6)). Additional hydrogen will be produced during the WGS reaction.



### 3.3. CO<sub>2</sub> capture

Although carbon dioxide is neutral during the whole process of biomass growth and utilization, it still needs several years to complete the process of carbon dioxide revivification. That means the carbon dioxide emitted from biomass fuel processor will exist as greenhouse gas for a considerably long time. To further control the greenhouse gas emission, carbon dioxide capture system could be coupled with the biomass fuel processor. With CO<sub>2</sub> captured, the bio-energy system will achieve the state of negative CO<sub>2</sub> emission, which has great potential to mitigate the global warming. The captured CO<sub>2</sub> could be collected and stored in

geological media, such as oil and gas reservoirs and deep saline aquifers [60–63].

Different kinds of materials and methods have been reported for CO<sub>2</sub> capture. Calcium-based materials, such as CaO–CaCO<sub>3</sub> and Ca(OH)<sub>2</sub>–CaCO<sub>3</sub>, are particularly suitable sorbent for CO<sub>2</sub> capture at temperature and pressure conducive to the biomass fuel processors. These materials were proved to be able to absorb CO<sub>2</sub> effectively. Solar energy or low quality exhaust heat could be used to regenerate the absorption materials to maximize the system utilization. Florin [63] carried out thermodynamic analysis based on experiment of hydrogen generation by steam reforming of biomass, coupled with in situ CO<sub>2</sub> capture. Within the temperature range of 800–900 K, steam-to-biomass ratio of 1.5 and sorbent loading of Ca:C of 0.9 were shown to be effective CO<sub>2</sub> capture and maximum H<sub>2</sub> output [63]. Zhang et al. [60] developed a two-section reactor model to describe the steam methane reforming reactor, with high-temperature CO<sub>2</sub> adsorption embedded. Nikulshina et al. [61] analyzed the thermodynamics of a solar thermochemical cycle for the capture of CO<sub>2</sub> with Ca(OH)<sub>2</sub>–CaCO<sub>3</sub> cycle system. Weimer et al. [62] investigated the process for simultaneous hydrogen production and CO<sub>2</sub> capture. The system consisted of two coupled reactors: (1) a gasifier using CaO to absorb CO<sub>2</sub> to produce hydrogen-rich product gas and (2) a regenerator using sorbent to produce high-purity CO<sub>2</sub> gas stream suitable for storage.

#### 4. Catalysts for biomass-derived fuel processing

The catalysts used for fuel processors can be divided into four categories: oxide catalysts, noble metal catalysts, base metal catalysts, and enzymes [64–70]. Their main advantages and disadvantages are summarized in Table 4. Systems using metal-based catalyst have been studied for decades and are still receiving much research interest. Meanwhile, the biological enzyme for fuel processing is in its early R&D stage and needs further development. It could be a promising alternative to enhance the biomass reforming process in the future.

##### 4.1. Noble metal-based catalysts

Noble metal catalysts, such as Rh, Ru, Pt and Pd, are widely used in biomass steam reforming, partial oxidation, and autothermal reforming because of their high activity, selectivity, and conversion rate. However, their costs are high. Several research works have been done on noble metal-based catalytic reforming of alcohols. It was found that Rh generally had the best performance among all noble metals. For steam reforming of alcohols, Cavallaro et al. [66] reported that Rh/Al<sub>2</sub>O<sub>3</sub> had the best catalytic performance in terms of ethanol conversion and hydrogen production at both high and low loadings. The Ru/Al<sub>2</sub>O<sub>3</sub> with 5 wt% loading could completely convert ethanol into hydrogen rich gas with hydrogen selectivity

above 95%. Galvita et al. [70] studied the decomposition of ethanol steam reforming over Pd support on a porous carbonaceous material and found that the catalyst exhibited a high activity and long-term stability. In general, the ethanol steam reforming reactivity of noble metals decreased in the following order: Rh > Pd > Pt [72].

The noble metal-based catalysts were also used in partial oxidation of biomass fuels. Silva et al. [73] investigated the partial oxidation of ethanol catalyzed by Ru/Y<sub>2</sub>O<sub>3</sub> and Pd/Y<sub>2</sub>O<sub>3</sub> over 473–1073 K. The results showed that the reaction route depended strongly on the type of metal. Ru achieved a hydrogen selectivity of about 59% and it was more suitable for H<sub>2</sub> production than Pd. In a more recent research, Silva et al. [74] investigated partial oxidation of ethanol and water–gas shift reaction in an integrated system for hydrogen production with Rh/CeO<sub>2</sub> catalyst. The results further revealed that hydrogen production was strongly affected by the reaction temperature. It also indicated that Rh/CeO<sub>2</sub> catalyst reached higher catalytic activity over the Pt/CeO<sub>2</sub> catalyst over a wide range of temperature.

There are limited literatures on the noble metal-based catalytic reforming of biogas. This is because the much economical non-noble metal-based catalysts already have satisfactory performance on reforming of methane in most of the operating conditions. However, noble metal-based catalysts are still dominant in biogas reforming at low temperature.

##### 4.2. Non-noble metal-based catalysts

Non-noble metal-based catalysts, which could be classified as base metal catalysts and oxide catalysts, are also common catalysts for biomass fuels reforming. Ni-based catalysts are proved to be suitable catalysts for most biomass-derived fuels reforming (SR, POX, ATR, and dry reforming). Muradov et al. [75] conducted the thermodynamic equilibrium calculations and experiment of biogas/landfill gas (CH<sub>4</sub> and CO<sub>2</sub> mixture) steam reforming and autothermal reforming over Ni-based catalyst. The hydrogen yield could reach 50% at 1123 K. Although deactivation of catalysts due to carbon decomposition was observed during the study, it could be prevented by adding steam or oxygen to the feedstock. Additionally, the study indicated that hydrogen rich gas produced from CH<sub>4</sub> reforming catalyzed by Ni was economically feasible.

Nickel-based catalysts could be suitable for steam reforming of biomass at low temperature if properly designed. However, it is very difficult to reduce the supported nickel catalyst due to the strong interaction between nickel and support [76]. Therefore, some studies tried to develop efficient catalysts with high activity and high durability for low-temperature steam reforming processor. Seo et al. [76] used nickel catalyst supported on mesoporous alumina xerogel (A-SG) to produce hydrogen by steam reforming of methane and investigated the effect of the A-SG support. The results showed that the Ni/A-SG catalyst had a strong

**Table 4**  
Main advantages and disadvantages of catalysts.

Category	Typical example	Description	References
Oxide catalysts	MgO, Al <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> , ZnO, TiO <sub>2</sub> , La <sub>2</sub> O <sub>3</sub> , CeO <sub>2</sub> , Sm <sub>2</sub> O <sub>3</sub> , La <sub>2</sub> O <sub>3</sub> –Al <sub>2</sub> O <sub>3</sub> , CeO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> , MgO–Al <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> and V <sub>2</sub> O <sub>5</sub>	Normally good activity but low selectivity	[64,67]
Noble metal catalysts	Rh, Ru, Pt and Pd	Active, high selectivity but the cost is high	[51,66]
Base metal catalysts	Co-based (Co/ZnO etc.), Cu-based and Ni-based (Ni/Al <sub>2</sub> O <sub>3</sub> , etc.)	Co-based: good catalytic performance, but rapidly deactivate  Cu-based: good activity at low reaction temperature, while H <sub>2</sub> selectivity is poor Ni-based: high conversion and the H <sub>2</sub> selectivity, but may occur coke deposition and a severe deactivation	[47,49,68]
Enzymes	Gly 1–13 enzyme systems (to catalyze glucose and ethanol), Pyr 1–9 enzyme systems (to catalyze pyruvate)	Environmentally friendly and high efficient reaction at room temperature but limited lifetimes	[65,69,71]

resistance toward catalyst deactivation even at low operating temperature.

Other kinds of newly developed non-noble metal catalysts could also work well at low temperature. Lødeng et al. [77] investigated different metals and oxides over Co/Al<sub>2</sub>O<sub>3</sub> catalysts, including Ni, Fe<sub>3</sub>O<sub>4</sub>/Cr<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub> or K<sub>2</sub>O, etc., in catalytic partial oxidation of methane. Comparisons in methane conversion and selectivity were carried out in the temperature range of 473–1023 K at 1 atm in a continuous fixed-bed quartz reactor. The Co catalyst showed stable performance during a steady state at 923 K and extinguished at about 723 K. Before extinguished, the reaction was typically following thermodynamic equilibrium which is the highest achievement in theory. The study indicated that addition of oxides would promote instability and deactivation. Additionally, the performance of Ni catalysts was better than that of Co catalysts at low temperature. Fe-based catalysts showed combustion activity in the whole temperature range.

#### 4.3. Enzymes and bio-processing

Traditional biological production of hydrogen from biomass was achieved through fermentative or photofermentative microorganisms processes [78,79]. The major challenges for biological hydrogen production in fuel cell systems are to enhance the low yield from fermentative production and to reduce the reactor size for photofermentative production [80]. Recently, new technologies have been developed for the biological catalytic fuel processors.

Westermann et al. [80] suggested a concept namely bio/catalytic refinery (Fig. 4). It was a fuel processor that combined a biorefinery and chemical catalytic technologies for the production of multiple fuels (hydrogen, ethanol, and methane) and a yield of 10–12 mol hydrogen per mol glucose could be derived from biological waste [80]. This type of biological–chemical fuel processor is advantageous due to its high hydrogen yield to feed the fuel cell, high versatility with respect to input of different types of abundant and low-cost agricultural wastes.

Recent research has focused on biological hydrogen generation from biomass-derived fuels through biofuel processor which relies on biological molecules, such as enzymes. There are two types of biofuel processors: microbial-based and enzyme-based biofuel processors. More research has been done on microbial-based biofuel processor and it has demonstrated its importance in wastewater engineering [69]. The lower power density limits its further application in power generation and therefore it will not be discussed in detail here.

The enzyme-based biofuel processor, however, has wider potential applications and is presently under rapid development. An enzymatic biofuel cell is an integration of enzymatic biofuel processor and fuel cell. Unlike traditional fuel cells using catalyst for the electrochemical reaction, enzymatic biofuel cells may not have a membrane [69]. Low volumetric catalytic

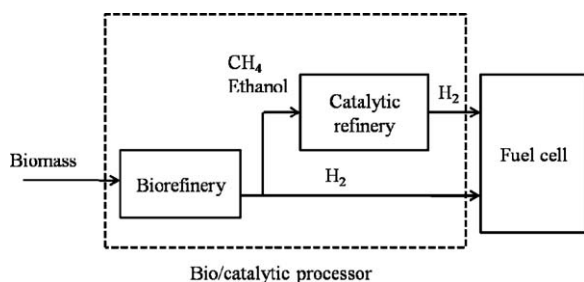


Fig. 4. Bio/catalytic conversion of biomass to hydrogen.

activity and low power density are the main problems of biofuel cells. These problems could be solved by enzyme isolation techniques to increase the volumetric activity, catalytic capacity as well as the output power density [65]. Additionally, enzymatic biofuel cells have the ability to increase the degree of oxidation because there are natural enzymes and enzymatic pathways to completely oxidize fuels. Alcohols, such as glycerol and ethanol, and glucose are the two major biomass fuels for enzymatic biofuel cell and they are receiving increasing research interest.

Liu [69] carried out investigation on a system of membraneless biofuel cell activated by enzymes (glucose oxidase and laccase). The fruit juice, such as grape, banana or orange juice, containing glucose was selected as the fuel. In the experiment, the biofuel cell worked effectively and revealed that the anode could work in air-saturated solution. The experiments demonstrated the potential to use biofuel cells to harvest energy directly from biomass, such as fruit juice.

Glycerol/O<sub>2</sub> enzymatic biofuel cell was investigated by Arechederra et al. [65]. In this study, the bioanodes have yielded a maximum power density of 1.21 mW cm<sup>-2</sup> at room temperature. They could operate at 98.9% fuel concentrations. The study indicated that the glycerol/O<sub>2</sub> biofuel cell had a higher power density compared with ethanol enzymatic biofuel cells due to its ability to oxidize the fuel more completely [65].

## 5. Biomass-derived fuel processor configurations

Early investigation and development of fuel processor were traditionally based on tabular, annular and fixed bed configurations employed in the catalytic industry for decades. Research has shown that the catalytic reactions of fuel reforming mainly take place at a very thin layer of the catalyst, especially for those fuels with short carbon chain. Thus, choosing a suitable fuel processor is one of the key factors to improve the energy efficiency. Besides, more compact configurations are to be developed to meet the demand of new applications of mobile fuel cell systems. It is important to develop fuel processors with high active surface-to-volume ratio, easy dynamic control and efficient heat transfer. Some typical newly developed processor configurations are illustrated in Fig. 5 and the details are discussed in the following sections.

### 5.1. Monolithic reactor

The monolithic reactor is composed of a substrate with interconnected repeating channels. The honeycomb substrate can be made of ceramic, metal or plastic. Ceramic is the most

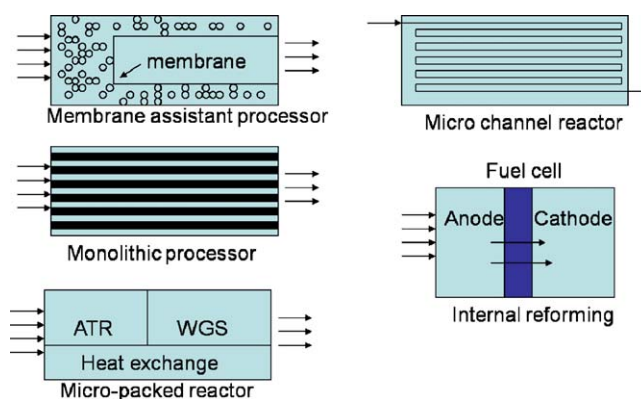
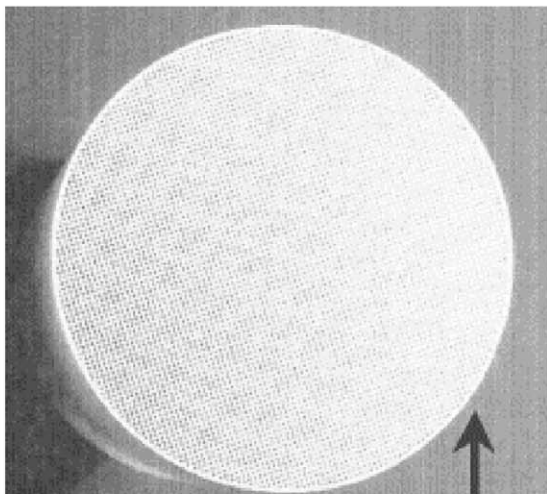


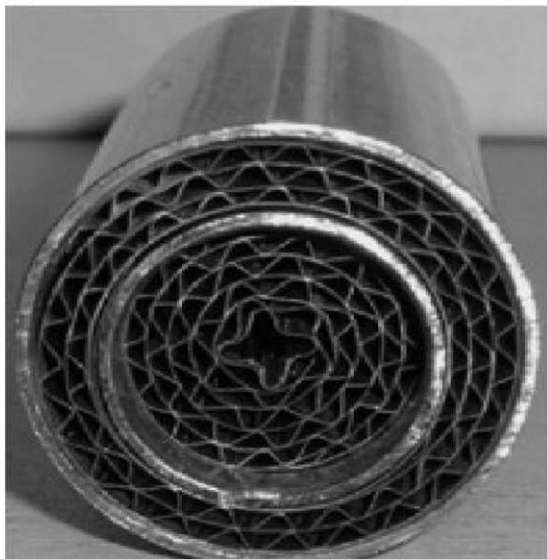
Fig. 5. Schematic of selected fuel processor configurations.



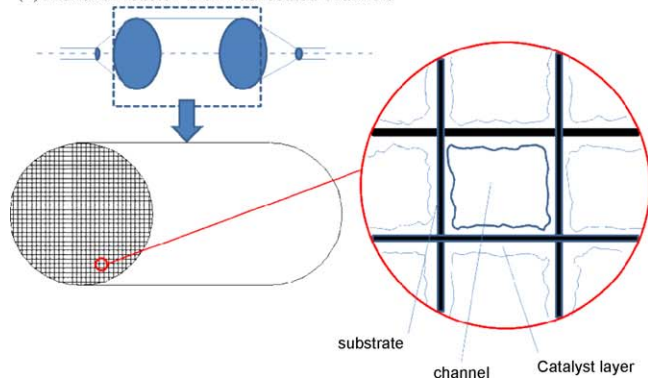
(a) Ceramic monolithic reactor [81]



(b) Metal monolithic reactor [82]



(c) Monolith reactor with washcoated channels



**Fig. 6.** Configuration and photographs of monolithic reactors. (a) Ceramic monolithic reactor [81]. (b) Metal monolithic reactor [82]. (c) Monolith reactor with washcoated channels.

commonly used material. The active catalyst is dispersed on the carrier which composed of a high surface area of inorganic oxide, such as  $\gamma\text{-Al}_2\text{O}_3$  [81–84]. Fig. 6 shows some typical ceramic and metal monolithic reactors.

Monolithic reactors are widely used in environmental applications, such as exhaust gas purification. Recently, some literatures report the studies of monolithic reactors for biomass-derived fuel reforming for fuel cell applications. Compact monolithic reactor provides a large active catalyst surface [81]. Moreover, it has a large frontal area and the pressure drop of the flow of fuel supply is low. Its light weight requires only a short start-up time to heat up the reactor to the activating temperature. The monolithic configuration is more tolerant to vibration and more stable. The abovementioned features fulfill well the requirements of biomass-derived fuel processing for fuel cell systems, especially for the portable and APU systems which need the on-site hydrogen supply. Table 5 lists the relevant research works on ceramic monolithic reactor of biomass-derived fuels.

Comparisons between biomass-derived fuel processing in monolithic and other kinds of reactors can be found in the literature. Liguras et al. [83,84] tested the performance of Ni and Ru catalysts on cordierite monolith, ceramic foams and  $\gamma\text{-Al}_2\text{O}_3$  pellets for POX of ethanol. The results showed that the ethanol reforming process had different  $\text{H}_2$  selectivity and system stability in different reformers. The cordierite monolith exhibited the best performance for a wide range of operating conditions and excellent long-term stability with low coke formation. Iojoiu et al. [85] investigated the monolith and powder as catalyst supports to reform bio-oil and found that the monolith catalyst supports could increase  $\text{H}_2$  productivity and stability by decreasing the side-product formation and improving the soot gasification.

Monolithic reactors have some shortcomings. They are adiabatic reactors which limit the control of temperature, especially for ATR of biomass-derived fuels. However, the use of metal monolith could improve the heat transfer inside the reactor and thus some investigators have carried out research using metal monolith with combined reforming and combustion of biomass-derived fuels. Mei et al. [82] tested a novel metal monolith reactor for coupling methane steam reforming with catalytic combustion. The combustion and steam reforming occurred in the inner pipe and outer pipe, respectively. The metal monolith yielded high performance as the heat was transferred between the endothermic and exothermic reaction sides. Thus, the energy utilization in the system could be maximized.

## 5.2. Micro-reactor

For small and medium fuel cell systems for portable and transportation applications, the size and weight of the fuel processor become critical factors. Thus, world-wide research has emphasized micro-reactors for fuel processing. The main features of micro-structured reactors are the high surface-area-to-volume ratio and high heat and mass transfer coefficients compared with the conventional chemical reactors [59].

There are two types of micro-reactors, namely micro-packed reactor and micro-channel reactor. The micro-packed reactor adopts a compact configuration with an integration of different functional parts, such as vaporizer, SR reactor, WGS reactor and heat exchanger. The micro-channel reactor employs channels with apparent diameter of a few microns to increase the active area for catalytic reforming. Comparatively, the latter has wider applications. Fig. 7 shows the configuration and photographs of micro-reactors.

Highly efficient catalysts are indeed needed for micro-reactors due to the required high throughputs in limited size. Noble metals with high catalytic efficiency, such as rhodium, palladium, and platinum, are usually adopted in micro-reactors. The contact time of the fuel and catalysts is a few milliseconds long. Besides noble metal catalysts, nickel-based and copper-based catalysts could be

**Table 5**  
Selected researches on ceramic monolithic reactor of biomass-derived fuels.

Reactions and fuels	Monolith geometry	Catalysts and supports	Results	References
POX of methanol	400 cpsi d16 × 22 mm	ZnO–Cr <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> –ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	MeOH conversion close to 100% and the CO content lower than 1.4%, no significant deactivation	[53]
POX of ethanol	400 cpsi	Ni/La <sub>2</sub> O <sub>3</sub> –γ–Al <sub>2</sub> O <sub>3</sub>	EtOH conversion near 100%, H <sub>2</sub> selectivity near 95%	[83]
SR of glycerol	–	Rh; Pt; Pd; Ir; Ru; and Ni	About 80% of H <sub>2</sub> selectivity, CH <sub>4</sub> production completely inhibited	[22]
ATR of methane	400 cpsi d35 × 35 mm	Ru/γ–Al <sub>2</sub> O <sub>3</sub>	CH <sub>4</sub> conversion of about 75%; The product gas: H <sub>2</sub> (65%), CO(5%)	[86]
Cracking and SR of bio-oil	1200 cpsi d20 × 17 mm	Pt/Ce <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub> and Rh/Ce <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub>	50% H <sub>2</sub> in the gas stream, high stability	[85]

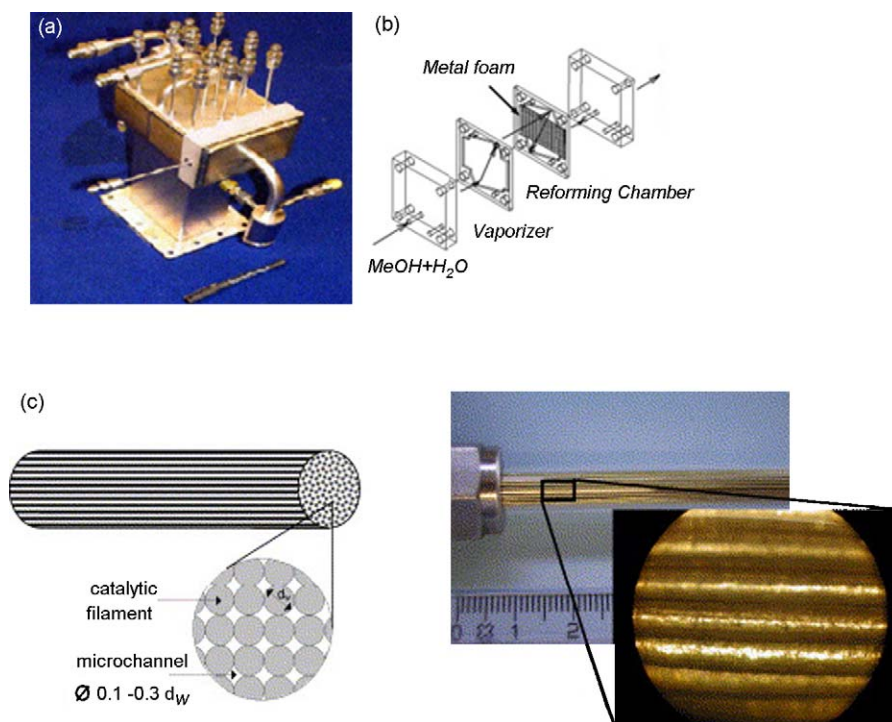
found in recent literature and good performance is reported [87]. The catalysts are usually impregnated on oxide supports to create micro-channels in the size of microns for hydrogen production with high efficiency. Metal and non-metal foams, including nickel foam, Raney nickel, alumina foam, FeCrAl foam and silicon foam etc., have been widely used as supports in micro-reactors [87]. Wash-coating, sol–gel, wetness impregnation, and chemical and physical vapor deposition can be employed to coat catalysts onto the foam supports [88].

Table 6 lists some useful references on micro-reactors with biomass-derived fuels. Among different biomass-derived fuels, bio-methanol and bio-ethylene glycol, which have high energy density, are the most suitable candidate fuel for micro-reactors. The size of micro-reactor has been reduced to a level suitable for most portable applications, such as notebook computers and cellular phones. The system efficiency and power density have increased remarkably over the past five years. Most of the earlier works used methanol as the sole fuel for micro-reactors. A 150-W micro-reactor using methanol as the fuel achieved a thermal efficiency of 78%, system electrical efficiency of 37%, power density of 2240 W/L, and fuel conversion of 95% [49]. In the recent years, more and more potential biomass-derived fuels were attempted as feedstock, such as biodiesel.

It should be noted that the micro-reactors have unique flow and heat and mass transfer properties, which need to be carefully investigated. Concluded from the literature, poor heat transfer efficiency, complex catalysts coating methods, frequent occurrence of over hot spots and comparatively low catalytic efficiency are the main obstacles to overcome in the development of the micro-reactor technology.

### 5.3. Internal reforming

Internal reforming of biomass-derived fuels could achieve higher efficiency than traditional fuel processor fuel cell systems. In an internal reforming system, the fuels are processed in a unit that is essentially an integral part of a fuel cell rather than in a separate reactor [59]. The reforming reaction takes place directly at the anode of the fuel cell without any external fuel processor, simultaneously with the charge transfer reactions that lead to electricity production [59]. Internal reforming has the following advantages: compact size, high efficiency, fast loading response and low cost. The internal reforming system can be further enhanced by using heat recovery in the fuel cell system. Since the hydrogen rich gas produced by internal reforming usually contains CO, it is more suitable for high temperature fuel cells, such as SOFC



**Fig. 7.** Sketched configuration and photos of micro-reactors [88,89]. (a) Fuel processor including micro-channel SR, fuel injector, and burner, reported in 2004; (b) sketched configuration of a micro-reactor using methanol as fuel; (c) compact string-reactor for ATR, consisting of a tube with a diameter in the centimeter range where thin metallic catalyst wires are introduced with diameters of 500 μm, reported in 2006.

**Table 6**  
Selected researches on micro-reactors with biomass-derived fuels.

Micro-reactor types	Output power and reactor size	Reactions and fuels	Catalyst and supports	Performance	References
Micro-channel	150 W size of 60 mm × 160 mm × 10 mm	SR of methanol	Cu/Zn/Al <sub>2</sub> O <sub>3</sub>	80% of methanol conversion	[90]
Micro-channel	10 W Size of 40 mm × 40 mm × 8 mm	SR of methanol	Cu/Zn/Al <sub>2</sub> O <sub>3</sub>	90% of methanol conversion; CO concentration 1.6%	[91]
Compact String reactor	Size <sup>a</sup> about d5 × 20 mm <sup>3</sup>	ATR of methanol	Cu/Zn/Al <sub>2</sub> O <sub>3</sub> modified by Cr/Cu-spinel	Methanol conversion of 91.5%	[89]
Tubular packed reactor	Size <sup>a</sup> smaller than 80 mm × 80 mm × 10 mm	POX of methane	Rh-based	CH <sub>4</sub> conversion near 80%, H <sub>2</sub> selectivity near 80%	[92]
Micro-channel	Size <sup>a</sup> about 50 mm × 50 mm × 5 mm	SR of methanol	Cu/Zn/Al powder catalyst;	Conversion near 100%	[93]
Micro-channel	Not reported	SR of biodiesel	Not reported	100% conversion of pure biodiesel	[17]

<sup>a</sup> The exact size of the reactor was not given in the literature. The values of size were evaluated from provided figures and photos.

which is carbon monoxide tolerable [59]. For low-temperature fuel cells, the catalysts should be selected carefully to control the CO selectivity at a very low level.

The internal reforming could be divided into two types: direct and indirect internal reforming, depending on the degree of contact between the reformer and the fuel cell electrode. Several investigations on internal reforming of biomass-derived fuel have been reported recently [25,37,94]. The research mainly focused on one-carbon fuels such as methanol and methane. Internal reforming of these fuels is advantageous due to easy control of the by-products. More recently, longer carbon chain fuels, such as ethanol and glycerol, also have received attention as they have lower crossover rate of the electrolyte, resulting in a greater potential to increase the efficiency.

Cavallaro et al. [94] used bio-ethanol as the fuel for an indirect internal reformer of molten carbonate fuel cells (IIR-MCFCs) with different catalysts. It was found that Co/Al<sub>2</sub>O<sub>3</sub> catalysts were suitable at higher loading of active phase (20 wt.%) but decayed in a short time due to coke deposition [94]; Rh/Al<sub>2</sub>O<sub>3</sub> catalysts showed high performance at both high and low loadings (5 wt.%). The MgO represented a more suitable support because of its low acidity with respect to time. The study concluded that the Co/MgO at high loading (20 wt.%) was the most suitable catalyst for bio-ethanol indirect internal reforming as its high performance and economical availability, when compared with noble metal, such as Rh.

Biogas internal dry reforming in SOFC was also reported by Goula et al. [25]. Ni-based cermet anodes and yttria stabilized zirconia (YSZ) solid electrolyte were studied and biogas with different CO<sub>2</sub>/CH<sub>4</sub> ratio was fed to the SOFC for testing. The study showed that the current and power densities of the SOFC were maximized for equi-molar CO<sub>2</sub>/CH<sub>4</sub> biogas composition. It also showed that SOFC with biogas internal reforming was stable and reliable over a wide range of CO<sub>2</sub>/CH<sub>4</sub> ratio feedstock.

## 6. Discussion

From the literature, it can be seen that most of the reported works on fuel processors were carried out with methanol, ethanol or methane as the fuel. All of them can be derived from renewable biomass in a carbon neutral manner. The chemical kinetics of reforming these short carbon chain fuels is usually easy to control, resulting in high fuel conversion efficiency and hydrogen selectivity.

However, deriving these fuels from biomass is rather expensive and difficult. For example, renewable methane can only be derived from biogas, which is strongly geographically dependent; bio-methanol is highly expensive and still not popular. Comparatively, long carbon chain fuels, such as biodiesel and vegetable oil, are much easier and more economical to produce from biomass. Some of them are already commercially available. The main problem of utilizing these fuels for fuel cell application is the occurrence of

unexpected side-reactions during the reforming process, resulting in deactivation of the catalyst system. Presently, limited literature can be found on successful reforming of these fuels in an efficient and steady manner. At the same time, the novel biomass-derived fuels with high energy density, such as ethylene glycol, are continually developed to satisfy the high level requirement of applications. Although these biomass-derived fuels are rather expensive, they are adopted in the applications that require high performance, such as military use. With the development of enzymatic technologies, biomass fuels, such as glucose, become potential fuels for hydrogen production. Further research should be done to develop these hydrogen production technologies for biofuel processor–fuel cell systems.

Catalyst is an important component of the fuel processor. The nature of the catalyst, its support, precursor, and preparation method can affect the catalytic performance. The literature indicates that Rh and Ni are commonly identified as the most suitable catalysts for steam reforming, partial oxidation and autothermal reforming of alcoholic fuels, including methanol, ethanol and glycerol. Rh-based catalysts are of higher activity for C–C rupture and selective to hydrogen when compared with other noble metal catalysts. Ni-based catalysts, however, can achieve comparable performance at a lower cost. Thus, it is a more promising candidate for fuel cell commercialization and has received more research interest recently. Ni-based catalysts are also reported as an ideal option for reforming of biomass fuels, varying from biogas to vegetable oil. Besides Rh and Ni, Pt, Cu and Ce are effective catalysts as well. Bi-metallic and alloy metal catalysts are also receiving increasing research interest. More attention should be paid on catalysts for reforming long carbon chain fuels to gain better understanding of their reaction mechanisms. At the same time, it can be seen from the latest literature that there is a research interest shift from noble metal-based catalysts to non-noble metal catalysts. It is reasonable to expect that the conventional noble metal-based catalyst systems for biomass fuel processing will be replaced by more economical alternatives, such as Pt-free catalysts, Rh-free catalysts and green catalysts.

Temperature, pressure and gas composition can seriously affect the catalytic reforming process. Thus, it is necessary to optimize the operating conditions for certain catalytic reactions. Many works have been done to investigate the optimal reforming conditions for various fuels and reforming types. However, it should be noted that the optimal condition for fuel reforming (e.g. high reforming temperature) may not be favorable for the subsequent carbon monoxide purification and fuel cell electro-chemical reaction, especially for low-temperature PEM fuel cells [76]. Additionally, the high temperature requires higher quality of construction materials and more complex configuration of fuel processor. It will also cause a longer response time for start-up and shut-down of the fuel processor. Generally, the biomass-derived



alcohols, such as ethanol and glycerol, require much lower reforming temperature than other biomass fuels. The biogas, composed of  $\text{CH}_4$ , has the highest operating temperature above 1273 K among the common biomass fuels. Therefore, there are needs to lower its reforming temperature ( $<1073$  K) [77]. Some studies have already been carried out using new catalysts to lower its reforming temperature. However, further reduction in temperature below 973 K would be much more difficult, mainly because of the unfavorable thermodynamics for partial oxidation products [77].

New technologies, such as enzyme catalysis,  $\text{CO}_2$  capture and micro-reactor, have potential for rapid development of fuel processor–fuel cell system due to their inherent advantages. For example, the enzyme catalysis has a much higher catalytic efficiency and better environmental performance than the metal-based catalysts. However, they are not expected to replace the conventional technologies in the foreseeable future before overcoming the major obstacles due to the short life time of the enzymes (commonly less than 20 days [95]).

Some biomass-derived fuel processors have already been developed for testing and demonstration for commercial use. A micro-electronic product powered by fuel cell system with enzymes activated internal reforming utilizes sugar as a biomass fuel [96]. Another successful product is designed with complete self-contained fuel processor integrated in fuel cell auxiliary power units (APUs) system, which could be powered with various fuels, including biomass fuels [97]. Therefore, it is reasonable to believe that the fuel processing technology will be developed to mature stage in the near future.

## 7. Conclusion

Biomass fuel processor is an important alternative to conventional fuel processor to supply hydrogen or hydrogen rich gas to fuel cells. Fuel cell coupled with biomass-derived fuel processor is one of the most promising energy providers in the future. It is renewable, environmentally friendly and carbon neutral. Numerous types of biomass-derived fuels, including ethanol, biodiesel, glycerol and biogas, could be the feedstock for a fuel processor. Each biomass fuel could be converted in the processor under different types of reforming, such as autothermal reforming, steam reforming and partial oxidation. The biomass conversion and hydrogen selectivity could be high (near 100%) for most of the biomass-derived fuels if the reforming system is well designed. Both catalyst and operating condition play an important role in the fuel processor.

Newly developed relevant technologies include low-temperature reforming technology, novel reformer configurations, internal reforming, carbon dioxide capture coupled technology and enzymatic biofuel processor. They can enhance the biomass fuel processor–fuel cell systems substantially and broadly expand their applications.

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