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CRITICAL REVIEW

Towards reforming technologies for production of hydrogen exclusively from renewable resources**Olusola O. James,^{*a,b} Sudip Maity,^b M. Adediran Mesubi,^a Kehinde O. Ogunniran,^a Tolu O. Siyanbola,^a Satanand Sahu^b and Rashmi Chaubey^b***Received 16th December 2010, Accepted 14th June 2011*

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Stern standards on the quality of hydrocarbon fuels, particularly on sulphur and aromatic content, is one of the major drivers of increasing hydrogen demand by petroleum refineries. The fuel standards are often predicated on reducing environmental pollution. However, most commercial hydrogen production processes are based on non-renewable resources which are associated with high carbon footprints. With increasing demand of hydrogen, the carbon footprint associated with hydrogen production will increase accordingly. Incentives for green hydrogen production technologies will be an impetus toward smooth succession of industrial processes from high to low carbon footprint. It will engender a shortened learning curve and facilitate entry of green reforming technologies into the hydrogen market. This review examines the potential of some emerging reforming technologies for hydrogen production from renewable resources.

1 Introduction

The present global energy system is largely based on chemical fuels. It is built around hydrocarbon compounds from fossil fuels (petroleum, coal and natural gas) as energy carriers. Fossil fuels are non-renewable energy resources and there has been increasing awareness on the depletion of petroleum

reserves. Moreover, increasing energy demand and continued use of fossil fuels have raised concerns about environmental pollution, global warming and consequences of global climate change.¹⁻² Hence, there has been a quest for energy carriers from renewable sources that can replace the present hydrocarbon compounds from fossil fuels. To this end, there has been increasing attention on hydrogen as a renewable and environmentally friendly energy carrier, and as a viable replacement for hydrocarbon compounds in the future.³⁻⁶ Thus, a paradigm shift from the present hydrocarbon energy economy to a hydrogen energy economy (simply hydrogen economy) is envisaged.⁷⁻⁹

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In this report we attempt to highlight debates about the hydrogen economy and assess the hydrogen demand situation and its direction in the near future. With the notion that realisation of a hydrogen economy hinges on economic production of hydrogen from renewable resources, we draw from the present commercial hydrogen production, steam methane reforming (SMR), and focus on reforming technologies as viable routes to renewable hydrogen. We briefly describe SMR in order to appraise efforts at reducing its carbon footprint. We seek to draw attention to the effect that present approaches to reduction of the carbon footprint associated with SMR do not seem to lead to a significant reduction in greenhouse gas emission. This contribution is therefore intended to stress that the quest for renewable hydrogen production needs to be approached from the use of renewable inputs. In the end, we explore emerging reforming technologies that have potentials for this purpose and make suggestions for their improvement.

The idea about a hydrogen economy has attracted opposing views on its merits and sustainability.¹⁰⁻¹² On the one hand, advocates of a hydrogen economy argued that the efficiency of combustion of hydrogen in fuel cells is higher than the efficiency of burning hydrocarbons in combustion engines. Combustion of hydrogen produces only water while hydrocarbon combustion releases carbon dioxide and other air pollutants. Thus, replacing hydrocarbons with hydrogen as energy carrier will reduce and eventually eliminate carbon dioxide emission.¹³⁻¹⁴ On the other hand, argument against hydrogen economy is centred on its feasibility. It was argued that although hydrogen is the lightest and the most abundant element, hydrogen is a synthetic energy carrier, it does not exist in the free state in nature, it has to be extracted from its compounds, the most common and carbon-free being water. It was explained that based on the law of thermodynamics the net energy value of hydrogen from water through electrolysis is negative. It was argued further that because of the physical properties of hydrogen,



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infrastructural requirement for its production, storage, transportation and utilisation are such that the well-to-wheel efficiency of a hydrogen-based energy system will be very low when compared to the present hydrocarbon system or a system that is based on electricity.^{15–18}

Perhaps the reality of the aforementioned issues about the sustainability of the hydrogen economy may account for the delay and reduced enthusiasm about widespread adoption of fuel cell vehicles. However, regardless of the arguments on a hydrogen economy, global demand for hydrogen has continued to increase and an annual growth rate of 3.4 percent had been predicted through 2013. Reports on market analysis indicated that the increasing global demand for hydrogen is mainly being driven by petroleum refineries. The rising hydrogen demand by petroleum refineries is traceable to stringent specification on fuels in recent times. In developed countries, as part of measures to control or minimise air pollution from hydrocarbon fuels, legislations stipulate low sulphur and aromatic content in fuels. The petroleum refineries operations to be employed to satisfy these requirements consume additional hydrogen input. This policy of stringent standards on fuels is spreading to emerging economies and other developing countries. Moreover, the Asia/Pacific region is currently witnessing rapid economic growth which is associated with increasing industrialisation, modernisation and expansion of existing infrastructures. In order to sustain their economic growth, energy consumption in this region will continue to increase along with expansion of petroleum refining capacities.¹⁹ As part of efforts toward attaining some measure of independence in hydrocarbon supply, coal-to-liquid fuels (CTL) projects are at different stages of commencement in China and in India. In the coal-based Fischer–Tropsch process/CTL, the syngas from coal is hydrogen deficient ($H_2/CO \sim 1.0$), this limits the amount of carbon in the syngas feed that can be converted to hydrocarbon. If higher carbon utilisation is desired, additional hydrogen input will be required. Thus, the implementation of CTL projects in China and India may further increase hydrogen demand in this region. Therefore, irrespective of the reality of the hydrogen economy, global hydrogen consumption is on the increase and commercially viable technologies for hydrogen production from renewable resources are imperative.

For sustainable development, it is desired that the energy input and feedstock for hydrogen production are from renewable resources.^{20–27} Also, the technologies should be sufficiently efficient in terms of feedstock and energy input utilisation, as well as afford high hydrogen production rate. Although there are several reaction routes to hydrogen, generally reforming reactions have been found to afford high hydrogen production rate and steam reforming of hydrocarbon is considered to be the most favourable route to large scale production of hydrogen at present. As part of several efforts towards the transition from non-renewable to renewable energy systems, reforming reactions using renewable resources are being developed and attempts to modify existing commercial reforming reactions are also being made to reduce their carbon footprints. Before we examine emerging reforming technologies for hydrogen production from renewable resources in the effort towards sustainable routes to hydrogen, we first appraise briefly steam methane reforming (SMR) and attempts at reducing its carbon footprint.

Table 1 Composition of steam reforming catalysts^{28–34}

Components	Examples
Active metal	Ni, precious metals (Rh, Pt, Pd, Ir)
Promoters	Mg, Ca, La_2O_3
Supports	Al_2O_3 , SiO_2 , CeO_2 , ZrO_2

2 SMR and attempts at reducing its carbon footprints

The main reactions in SMR are:



The thermodynamic conditions for high conversion include: high temperature, high steam/carbon ratio (about 2.5 for methane) and pressure range of 25–30 bar. Temperature as high as 850–950 °C may be required to achieve high methane conversion. A typical steam reforming catalyst is made up of an active metal and one or more promoters on a high surface area refractory material. The compositions of common steam reforming catalysts are listed in Table 1. The precious metal-based catalysts are more active and stable at the steam reforming conditions than the nickel-based catalyst. Because of the high cost of the precious metal, nickel-based catalysts are the universal industrial catalysts for SMR.

Although SMR is an established commercial hydrogen production technology, improvements in its processes and unit operations are still a strategic goal for improved process economy. A recent advanced SMR plant was reported to have attained 94–95% thermal efficiency.³⁵ In spite of the high hydrogen production rate and the attained energy efficiency, SMR still has the following drawbacks:

- The reaction is highly endothermic, it requires large amount of energy input and the catalysts are highly susceptible to deactivation at high reaction temperatures;
- Hydrogen production through SMR is associated with high carbon footprint since both the feedstock and energy input are from non-renewable sources;
- The number of unit processes and operations involved are rather a lot, which translates into huge capital investment.

The hydrogen needs of petroleum refineries are usually met by on-site hydrogen production units as part of the refining operations through steam reforming technology using hydrocarbon feedstocks and energy input. In 2008, petroleum sector and global hydrogen consumption were 364.1 and 409.1 billion cubic metres, respectively. It is also estimated that global hydrogen demand will increase by 73 billion cubic metres in 2013 and 41.25 billion cubic metres of hydrogen is projected to be produced outside the refineries. In light of the search for means of reducing greenhouse gases and carbon footprints of industrial processes,³⁶ the projected hydrogen supply from outside the refineries can constitute a strategic target to facilitate the entry of reforming technologies for hydrogen production from renewable resources into the hydrogen market.

Along with the goal of hydrogen production from renewable resources, efforts are also being made at reducing the carbon footprint of SMR. The high endothermic nature of steam

Table 2 Comparison of dry-reforming and steam reforming⁴⁵⁻⁴⁶

	Dry-reforming	Steam reforming
Reforming	$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ $\Delta H^\circ_{298} = +247.4 \text{ kJ mol}^{-1}$	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ $\Delta H^\circ_{298} = +206.2 \text{ kJ mol}^{-1}$
WGS	$2\text{CO} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 2\text{H}_2$ $\Delta H^\circ_{298} = -41.2 \text{ kJ mol}^{-1}$	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ $\Delta H^\circ_{298} = -41.2 \text{ kJ mol}^{-1}$
Net reaction	$\text{CH}_4 + \text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 4\text{H}_2$ $\Delta H^\circ_{298} = +165 \text{ kJ mol}^{-1}$	$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$ $\Delta H^\circ_{298} = +165 \text{ kJ mol}^{-1}$

Table 3 Comparison of tri-reforming and auto-thermal reforming^{46,47-49}

	Tri-reforming	Auto-thermal reforming
Dry reforming	$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ $\Delta H^\circ_{298} = +247.4 \text{ kJ mol}^{-1}$	
Steam reforming	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ $\Delta H^\circ_{298} = +206.2 \text{ kJ mol}^{-1}$	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ $\Delta H^\circ_{298} = +206.2 \text{ kJ mol}^{-1}$
Partial oxidation	$\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$ $\Delta H^\circ_{298} = -35.6 \text{ kJ mol}^{-1}$	$\text{CH}_4 + \frac{3}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$ $\Delta H^\circ_{298} = -519 \text{ kJ mol}^{-1}$
Oxidation	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ $\Delta H^\circ_{298} = -880 \text{ kJ mol}^{-1}$	
Overall	$4\text{CH}_4 + \frac{5}{2}\text{O}_2 \rightarrow 4\text{CO} + 7\text{H}_2 + \text{H}_2\text{O}$	$2\text{CH}_4 + \frac{3}{2}\text{O}_2 \rightarrow 2\text{CO} + 3\text{H}_2 + \text{H}_2\text{O}$
Net reaction	$\text{CH}_4 + \frac{5}{8}\text{O}_2 \rightarrow \text{CO} + \frac{7}{4}\text{H}_2 + \frac{1}{4}\text{H}_2\text{O}$ $\Delta H^\circ_{298} = -115.5 \text{ kJ mol}^{-1}$	$\text{CH}_4 + \frac{3}{4}\text{O}_2 \rightarrow \text{CO} + \frac{3}{2}\text{H}_2 + \frac{1}{2}\text{H}_2\text{O}$ $\Delta H^\circ_{298} = -156.4 \text{ kJ mol}^{-1}$

reforming is a result of the thermodynamic constraints of the high bond dissociation energy of its reactants. Coke formation and catalyst deactivation in steam reforming are governed by the kinetics of the elementary steps involved in the reaction. Several researchers have approached improving the performance of the steam reforming process from thermodynamic and kinetic perspectives.^{35,37-42} On the whole, the strategies adopted were towards maximising the hydrogen yield, the process inputs are still from fossil fuels. Direct attempts towards reducing carbon footprint in SMR is discussed vis-à-vis the use of CO_2 or CO_2 -steam mixture instead of steam and the use of non-thermal energy inputs and electrochemical reactor systems in modified steam reforming reactions.

2.1 Dry- and tri-reforming

Dry-reforming involves the use of CO_2 in place of steam for reforming of methane. Dry-reforming is more endothermic than steam reforming and catalysts are highly susceptible to deactivation by coke formation, like in steam reforming. The intention of the advocates of dry-reforming is that it creates an avenue for utilisation or reduction in CO_2 emission.⁴³⁻⁴⁴ It was reported that the H_2/CO ratio of syngas from dry-reforming is just what is required for Fischer–Tropsch synthesis. On the contrary, the H_2/CO ratio (unity) is less than what is commonly used in most commercial Fischer–Tropsch plants (H_2/CO ratio, 1.5–2). In addition, dry-reforming will require special infrastructures for generating pure CO_2 , which will add to the cost of hydrogen production. This may account for why dry reforming is unattractive for large scale production of hydrogen. In order to make dry-reforming industrially attractive, it was modified into what is known as ‘tri-reforming’. Here, three reactions are designed to take place simultaneously in

the reactor. It involves coupling dry and steam reforming (endothermic) reactions with methane oxidation (exothermic) reaction. The argument in favour of tri-reforming was that it could afford a cost effective process for producing syngas feed that is suitable for Fischer–Tropsch synthesis. Direct use of flue gases from power plants without prior treatment of the effluent was suggested as a cheap co-feed input with methane in tri-reforming.⁴⁷⁻⁴⁹

The reactions leading to hydrogen in dry- and tri-reforming are presented in Tables 2 and 3, respectively. Although the energetics of the net reactions in Table 2 are the same, assuming stoichiometric yield of hydrogen as presented in the net reactions, hydrogen output per molecule of methane is higher in steam reforming than in dry-reforming. In the absence of kinetic limitations, the difference in hydrogen output is only attributable to the oxidant use for reforming methane. Steam (H_2O) contains a lower proportion of oxygen atoms and also contributes to hydrogen output, whereas CO_2 contains a higher proportion of oxygen atoms and has no hydrogen. The use of steam favours higher hydrogen output per molecule of methane compared to using CO_2 . Since the carbon balance is unaffected by the use of either CO_2 or H_2O for reforming methane, it appears that dry-reforming does not offer any advantage over steam reforming in reducing CO_2 emission. To achieve the same hydrogen output in dry reforming and steaming reforming, higher amount of methane is needed in dry reforming with a corresponding higher amount of CO_2 output compared to steam reforming. Thus, it can be said that the use of CO_2 in place of steam does not translate into a reduction in CO_2 emissions.

Critical examination of tri-reforming revealed that it is very similar to autothermal reforming in concept. In the two processes, the feed compositions need to be strictly controlled throughout the reaction in order to maintain a steady reaction

Table 4 Comparison of electrochemical oxidation and internal reforming of methane

	Methane oxidation in SOFC	Internal reforming in SOFC
Anode		
1	$\text{CH}_4 \rightarrow \text{C} + 4\text{H}$	$\text{CH}_4 \rightarrow \text{C} + 4\text{H}$
2	$4\text{H} + 2\text{O}^{2-} \rightarrow 2\text{H}_2\text{O} + 4\text{e}^-$	$4\text{H} \rightarrow 2\text{H}_2$
3	$(1-x)\text{C} + 2(1-x)\text{O}^{2-} \rightarrow (1-x)\text{CO}_2 + 4(1-x)\text{e}^-$	
4	$x\text{C} + x\text{O}^{2-} \rightarrow x\text{CO} + 2x\text{e}^-$	$\text{C} + \text{O}^{2-} \rightarrow \text{CO} + 2\text{e}^-$
Cathode		
5	$(2-\frac{1}{2}x)\text{O}_2 + 2(4-x)\text{e}^- \rightarrow (4-x)\text{O}^{2-}$	$\text{CO}_2 + 2\text{e}^- \rightarrow \text{CO} + \text{O}^{2-}$
Net reaction		
6	$\text{CH}_4 + (2-\frac{1}{2}x)\text{O}_2 \rightarrow (1-x)\text{CO}_2 + x\text{CO} + 2\text{H}_2\text{O}$	$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$

where $0 \leq x \leq 1$

temperature, maximise hydrogen selectivity and to minimise coke formation. From Table 3, tri-reforming and autothermal reforming gave syngas with H_2/CO ratios of 1.75 and 1.5 respectively. The ratios are within the range required for Fischer–Tropsch synthesis and other industrial applications. But in spite of the slightly higher H_2/CO ratio of syngas from tri-reforming compared to autothermal reforming, tri-reforming could be less industrially attractive because its feed gas inputs are more and monitoring their composition is more complicated. Even if flue gases from the thermal plant are used as feed in tri-reforming as suggested, it may require additional purification facilities for removal of SO_x , NO_x and particulates. This will add to the cost and technical challenges of monitoring feed gas composition and may negate the supposed advantage of the proposed use of flue gas effluent from thermal plants. Table 3 also shows that the net reaction in tri-reforming and autothermal reforming is essentially partial oxidation of methane. It is clear that methane is the hydrogen substrate in the two net reactions and it appears that the H_2/CO ratio and the enthalpy of the net reactions are trade-offs, thus the advantage of inclusion of CO_2 is less apparent.

2.2 Electro-catalytic dry-reforming and current-enhanced steam reforming

Since the phenomenon of catalysis is electronic in nature, it had been conceived that if catalytic reactions are carried out electrochemically, it could lead to significant improvements in the reaction kinetics and process thermal efficiency.^{59–59} The use of electrochemical reactor systems for reformation of methane had been found to improve the reaction kinetics in terms of reducing coke formation and increasing catalyst life-span.^{60–62} This process is referred to as ‘internal reforming’. The electrochemical reactor is a solid oxide fuel cell (SOFC), a three phase boundary system which could be represented as follows:

Anode/Electrolyte/Cathode

Catalyst electrode/Solid electrolyte/Counter electrode

Ni-base reforming catalysts (*e.g.* Ni/ Al_2O_3)/typically Y_2O_3 stabilised ZrO_2 (YSZ)/oxide ion conductors (*e.g.* mixed metal oxides)

Internal reforming occurs at the same temperature as dry reforming of methane. The SOFC reactor system in internal reforming generates electrical power like a typical electrochemical cell along with production of syngas as the main reformates. The rate of catalyst deactivation in internal reforming is significantly reduced compared to dry reforming. This was attributed to cleaning-up of the coke carbon formed on the surface of the catalyst during the reaction by oxide ions which are electrochemically pumped from the cathode through the electrolyte to the catalyst (anode).⁶³ Although internal reforming normally occurs at the same temperature as dry reforming, the improvement in the reforming kinetics attributed to the reactor system employed could draw further attention to this reaction arrangement. According to James and Steven,⁶⁴ electrochemical oxidation of methane at the anode in a SOFC system produces electricity, water and carbon dioxide. Based on results of transient response studies, these authors proposed the following sequence of reactions at the anode: CH_4 decomposition; electrochemical oxidation of hydrogen and carbon to water and carbon oxides ($\text{CO}_2 \gg \text{CO}$), respectively. A similar investigation has not been reported for internal reforming of methane; however, a sequence of electrochemical reactions which are consistent with the product obtained in dry reforming may be suggested. But a detailed mechanistic study of the elementary reactions at the respective electrodes in internal reforming is necessary to confirm the suggestions. The respective electrode reactions for electrochemical oxidation and internal reforming of methane are presented in Table 4.

The above illustrates a strategy for achieving improvement in the kinetic of vapour phase reforming of hydrogen substrate (methane) with carbon dioxide using an electrochemical reactor system. In another report, Quanxin and co-workers achieved both kinetic improvement and lowering of reaction temperature in steam reforming of oxygenated organic compounds in a reactor system which looked like an electrolytic cell. Their reaction set-up is shown in Fig. 1. An electrified Ni–Cr wire was entwined around a quartz column packed with Ni/ Al_2O_3 catalyst. When a specified amount of alternating current (AC) was passed through the Ni–Cr wire, it heats up the catalyst bed and at the same time supplies electrons unto the catalyst. This reactor system was reported to operate at lower temperature, with higher carbon conversion and hydrogen yield, and improved catalyst stability than in conventional steam reforming (CSR) approach.

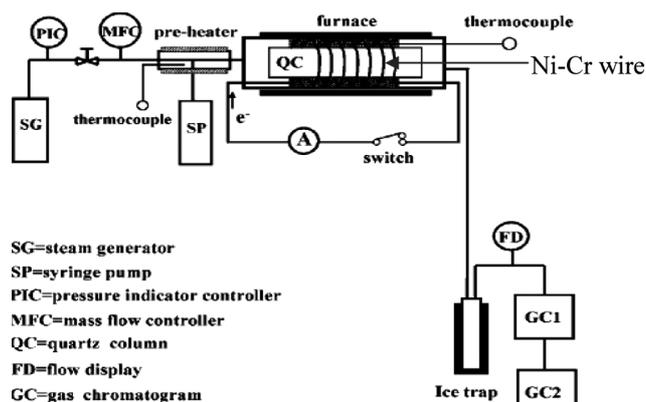


Fig. 1 Schematic setup of the fixed-bed flow reaction system for current enhanced steam reforming being pioneered by Quanxin and co-workers.⁶⁵

The authors explained that thermionic emission of electrons occurred from the Ni–Cr wire when it is electrified. The emitted electrons promoted the dissociation of the reactant (oxygenated hydrocarbons and water) as well as the reduction of the oxidised active metal clusters (NiO) in the catalyst. This combined effect accounts for the observed higher hydrogen yield in the current enhanced system compared to CSR.^{65–68}

The highlighted current enhanced steam reforming system is being pioneered by Quanxin and co-workers. They described the reaction as electrochemical reforming in two of their reports. An assessment of this reaction set-up revealed the arrangement is not consistent with the electrochemical description. When the reaction set-up is compared with the internal reaction reactor (dry reforming in SOFC system) described earlier, it is difficult to sort the reactor set-up into the components of an electrochemical cell (anode, cathode and electrolyte) and an AC was employed. It is also difficult to represent the reactions with formal electrochemical equations. In another perspective, when the reaction set-up can be likened to a special form of single stage plasma reforming system (discussed in section 2.3) where thermionic electrons replace the plasma. Irrespective of the inconsistency in the description of the reaction, they demonstrated that the use of a non-conventional reforming reactor arrangement improves the kinetics of the reforming reaction. It also revealed that application of energy input or activation of the reactant through non-conventional thermal means have the potential to afford lower temperature reformation of hydrogen substrates.

2.3 Plasma reforming

Plasmas are streams of highly energetic atomic or sub-atomic species (electrons, ions, radicals and neutral atoms). These energetic species, especially electrons depending on their energy, can activate, dissociate or ionise reactants, thereby promoting their conversion. Application of plasma technologies in reforming reactions for hydrogen production has drawn considerable research attention in recent times. This is with a notion that the use of the energetic species of plasma for reformation of hydrogen substrates could lead to higher hydrogen yield than what is obtainable from conventional catalytic reforming reactions. Other motivations for plasma reforming include: fast start-up time, compatibility with wide range of substrate (hydrocarbons as well as oxygenates), elimination of the use of catalyst or minimisation of catalyst deactivation, and compactness.⁶⁹

The conception of plasma as a more efficient energy input than conventional thermal energy for hydrogen production is yet to yield expected results. Energy efficiency and hydrogen selectivity have remained major challenges in plasma reforming. Plasma reforming generally displays lower hydrogen selectivity compared to conventional catalytic reforming reactions.⁷⁰ Although a number of reports have indicated that plasma reforming of oxygenated hydrogen substrates is more selective to hydrogen than hydrocarbon substrates, the energy efficiencies obtained in plasma reforming to date are still lower than the thermal efficiency already attained in advanced steam reforming.^{71–73} However, it is anticipated that the combined advantages of plasma and conventional catalytic reforming could be exploited by a synergy of the two processes. In order to maximise the integration, it is imperative to obtain insight about the best or optimum configuration for the coupling of the two technologies. An excellent review in this regard was reported by Hsin *et al.*⁷⁴ These authors explained that non-thermal plasma is generally preferred over thermal plasma because of its lower energy consumption, yet theoretical energy consumption for the conversion of a unit amount of methane using non-thermal plasma is higher than that in conventional catalytic reaction for the reforming of methane. It was suggested that the coupling of plasma with catalyst should be designed in such a way that the catalysts plays a dominant role in the reforming while the plasma is used to effect vibrational excitation of the reactants. They explained that plasma not only activates the reactants, it enhances the dispersion and stability of the active metal sites. Thus a packed bed arrangement will boost energy efficiency of plasma-catalyst coupling. Fig. 2 shows the classification of

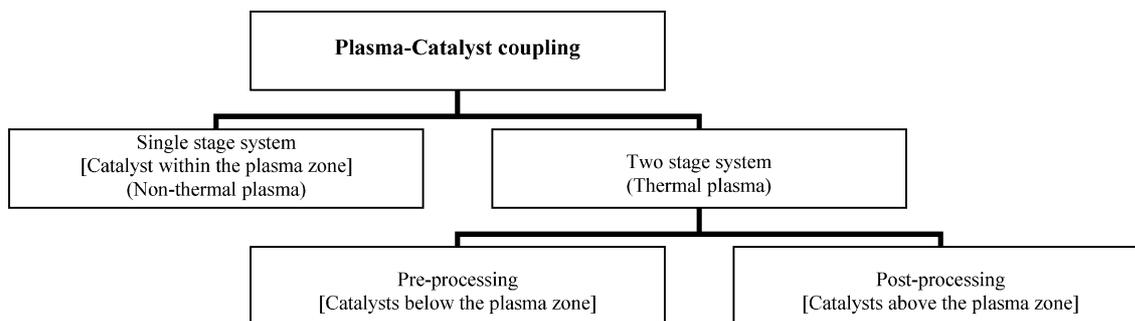


Fig. 2 Classification of plasma-catalyst coupling techniques for reforming of H-substrates for hydrogen production.

Table 5 Reaction conditions of APR and steam reforming of glycerol⁸⁴

Reaction conditions	Aqueous phase reforming	Steam phase reforming
Temperature	473–533 K	>673 K
Pressure	15–50 bar	1–2 bar
Reaction phase	Liquid	Vapour

plasma-catalyst coupling techniques for reforming reaction and the suggested plasma types for optimal performance.⁷⁴

In contrast to steam, dry and tri-reforming, where the reforming of hydrogen substrates occurs only in the gaseous phase, reformation of hydrogen substrate can be accomplished in the liquid phase using plasma reforming. This reduces the amount of energy input and also makes possible the use of hydrogen substrates with very low vapour pressure. Moreover, the quick start-up and ability to operate at ambient temperature and pressure makes plasma reforming suitable for small scale hydrogen production systems. Also the use of renewable hydrogen substrates can minimise overall carbon footprint associated with plasma reforming.

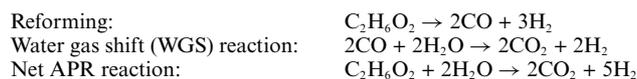
3 Reforming technologies for hydrogen production predicated on renewable resources

In this section, we examine reforming technologies for hydrogen production where the hydrogen substrates and/or the energy inputs are from renewable resources. We appraise their potentials and suggest strategies to improve them for large scale hydrogen production.

3.1 Aqueous phase reforming (APR)

Except plasma reforming, discussions on reforming technologies for hydrogen production up to this point are based on gaseous phase reactions. That is, the hydrogen substrates are in the gaseous phase. However, hydrogen production in systems where the hydrogen substrates are in the liquid state have also been shown to be possible. Aqueous phase reforming (APR) of water soluble substrates was pioneered by Dumesic and associates.^{75–76} The group carried out extensive studies on APR and pointed out that steam reforming of hydrogen substrates that have C/O ratio 1 are thermodynamically favourable at lower temperature (200–270 °C) than those of corresponding alkanes of the same carbon number. Generally, readily available hydrogen substrates (with C/O ratio 1) from carbohydrate biomass have low vapour pressures and a propensity to decompose at higher temperatures. APR is more suited for conversion of such substrates to hydrogen than steam reforming.⁷⁷ Moreover, the range of hydrogen substrates that can be converted to hydrogen through APR is being extended to include ethanol and cellulose.^{78–82}

In recent times increasing bio-diesel production has brought about production of glycerol in excess of its traditional uses. Thus, new applications that will lead to economic monetisation of the excess glycerol are being sought. Conversion of glycerol to hydrogen through APR is attracting research attention as a renewable hydrogen substrate.⁸³ Typical reaction conditions for APR and steam reforming of glycerol are presented in Table 5.



The contrast in the reaction conditions presents some advantages for APR over steam reforming. These include: lower energy input, minimised side reaction and catalysts deactivation rate, low CO selectivity in one pot reaction, easy hydrogen purification and CO₂ sequestration where necessary.^{84–85}

In order to consolidate the above-listed advantages of APR, a series of pilot-scale operations of hydrogen production through APR were carried out towards system optimisation and competitiveness with the already established SMR technology. There are a number of areas in APR that require improvements in this regard, especially in the area of catalyst development. To date, only group VIII metals have been explored as catalysts for APR. The order of hydrogen yields of these metals for APR and selectivity of supports investigated are as follows:

Metal activity: Pt > Ni > Ru ≈ Pd > Ir

Selectivity of support: Al₂O₃ > ZrO₂ > TiO₂

Pt/Al₂O₃ has emerged as the benchmark catalyst for APR but the high cost of Pt had motivated investigations on development of catalysts that are comparable in performance with Pt/Al₂O₃ from low cost group VIII non-precious metals.⁸⁶ But an accurate description of a reaction down to the atomic level is a prerequisite for the rational design of efficient catalysts for the reaction.

Using the simplest polyol with C : O ratio 1 : 1, ethylene glycol, Dumesic and co-workers⁸⁶ suggested that reforming of polyols like ethylene glycol does not require water. But water is a reactant for the water gas shift (WGS) reaction which increases hydrogen yield and drastically reduces CO selectivity.

Thus, the H₂/CO₂ ratio of 2.5 is expected at the reactor exit. However, the ratio is often less than this stoichiometric value, depending on the level of conversion and extent of side reactions. The reaction pathways and selectivity challenges in APR of polyols can be represented by Fig. 3. The series of elementary steps or catalytic site requirements for selective hydrogen formation are: dehydrogenation (O–H and C–H cleavage), C–C scission followed by WGS reaction. C–O cleavage is a critical route to

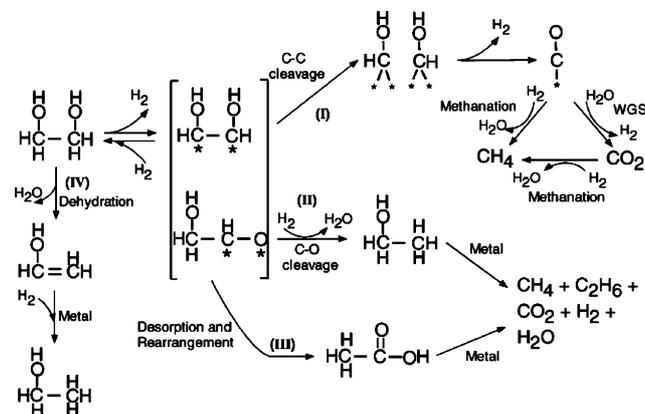


Fig. 3 Reaction pathways and selectivity challenges in APR of polyols.⁸⁶

Table 6 C–C scission, methanation and WGS activities of group VIII B metals

Activity	Decreasing order	Ref.
C–C scission	Ru \approx Ni > Ir \approx Rh > Fe \approx Co > Pt \approx Pd	109
Methanation	Co > Fe > Ru > Ni > Rh > Ir > Pt > Pd	110
WGS	Cu > Ru > Co > Ni > Pt > Pd > Fe > Rh	111

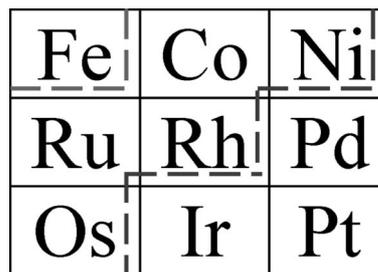
side reactions which decreases hydrogen selectivity. Other major side reactions include dehydration and methanation/Fischer–Tropsch synthesis (M/FTS). APR of polyols also takes place *via* a similar reaction scheme, however, the number of intermediates and complexity of the reaction increases with increasing carbon number.⁷⁸ Hence, catalyst design objectives for APR are to minimise C–O cleavage and maximise O–H, C–H and C–C cleavage activities.

APR and M/FTS, take place under similar reaction conditions. But catalytic site requirements, nature of reactants, products and reaction paths are opposite in each case. Moreover, there is increasing evidence in support of oxygenate intermediates in the M/FTS reactions.^{87–93} This may suggest that APR and M/FTS most probably share similar reaction intermediates and might explain why group VIII B metals are found to be active for the two reactions. However, M/FTS is a matured technology and has been studied extensively but APR is relatively in its infancy and is still open to a wide range of exploratory studies. If FTS can be delineated as reductive C–C coupling of CO mediated by hydrogen,^{94–96} then the reverse should be true for APR and it may be defined as dehydrogenative C–C decoupling of polyols or other oxygenate hydrogen substrates. Thus, based on the principle of microscopic reversibility of elementary reactions,⁹⁷ it may be inferred that catalyst development in APR will benefit from non-oxidative dehydrogenation and reverse engineering of M/FTS catalysts.

Recent reports have shown that basic sites^{98–101} or media¹⁰² promotes non-oxidative cleavage of C–H bonds. Moreover, acidic sites or media can promote undesired parallel side reactions (FTS, dehydration and rearrangement)^{76,103} which reduce hydrogen yield in APR. Thus, elimination of acidic sites and the presence of basic sites will not only facilitate the initial dehydrogenation of the substrate but also eliminate or minimise the extent of acidic sites catalysed side reactions. This agrees with reported higher catalytic activities and hydrogen selectivities obtained in the APR of glycerol over Pt supported on basic supports.^{104–105} Similar observation was also reported in APR of ethanol over hydrotalcite-supported Ni catalysts.¹⁰⁶ Presence of KOH has also been shown to increase hydrogen productivity in the APR of glycerol¹⁰⁷ and the use of KOH-modified aqueous solutions has also been demonstrated to afford CO_x-free hydrogen in a single reactor.¹⁰⁸

A keen examination of the reaction pathway in Fig. 3 reveals that M/FTS are consecutive reactions of CO and H₂ forming unwanted gaseous hydrocarbons. C–C scission and M/FTS occur on the metal sites. A cursory survey of C–C scission, methanation and WGS activities of group VIII B metals is presented in Table 6.

The mechanism and kinetics of syngas reaction over FTS active group VIII B metals has been related to the mode of CO

**Fig. 4** CO chemisorption on transition metals.¹¹² Dissociative chemisorption of CO at ambient temperature (top left), dissociative chemisorption of CO at 200–300 °C (between the dotted lines), non-dissociative chemisorption of CO at 200–300 °C (bottom right).

chemisorption on the metals (Fig. 4). Hydrocarbon formation was found to proceed *via* dissociative CO chemisorption.¹¹²

The trends in Table 6 and Fig. 4 show that the non-precious elements of group VIII B metals have higher C–C scission (Ni, Co & Fe) and WGS (Ni & Co) activities than Pt. These two activities are required for high APR performance. However, these metals displayed lower hydrogen yield than Pt. This suggests that the higher performance of Pt for APR compared to these metals is largely due to its lower M/FTS activity and stability. It also suggests that these metals have the potential to display higher performance for APR provided their M/FTS activities are reduced or eliminated. Special focus is on nickel because of its very high C–C scission activity. In agreement with the assertion above, reports have showed that modification of the metals between the dotted lines in Fig. 4 with those on the bottom right produced alloys or bimetallics which displayed higher APR performance than either of the starting monometallic catalysts. It has been shown that the performance of nickel for APR was significantly enhanced when alloyed with Pt or Sn as bimetallic catalysts. A report by Tanksale *et al.*,¹¹³ showed that co-impregnation of Pt with Ni (Pt : Ni = 1 : 12) on nanofibre alumina remarkably increases reducibility of Ni by alloy formation. Close contact between the two metals is essential for alloy formation. Sequential impregnation of Ni followed by Pt did not form alloy whereas alloy formation was obtained in the co-impregnated catalyst. Alloying of Pt with Ni was found to increase the number of active sites. This observation is not only similar but it is also a common practice in preparation of Co-based Fischer–Tropsch catalysts. In addition these authors believed that the alloy formation also decreased the CO chemisorption binding energy of Ni.¹¹⁴ Fuzhong *et al.*¹¹⁵ also demonstrated modification of Ni with Sn dramatically improves its performance for APR of ethylene glycol. Hydrogen selectivity as high as 98 mol% was reportedly obtained at high conversions. The Ni–Sn alloy catalyst was prepared by impregnation of skeletal Ni (RQ Ni) obtained by alkali leaching of rapidly quenched Ni₅₀Al₅₀ alloy with tin chloride solution. It was proposed that addition of Sn produces Ni–Sn alloy or assemblies on the catalyst surface which suppresses the undesired methanation reaction by blocking the active sites for CO adsorption and/or dissociation. They added that the presence of Sn promotes the desired WGS reaction by facilitating dissociation H₂O molecules.

Bimetallic APR catalysts were also reported by Dumesic and co-workers (Table 7).^{116–118} They found that PtNi, PtCo, PtFe and PdFe bimetallic catalysts, displayed higher activity and higher

Table 7 Performance of bimetallic APR catalysts compared to the corresponding monometallic counter-part^{117,118}

Active metal	Transition metal	Bimetallic catalyst	TOF _{H₂} (min ⁻¹)	Comparison with monometallic
Ni	Sn	RANEY®-NiSn	1.1, 1.4 with H ₂ selectivities of 47 and 93 for RANEY®-Ni, RANEY®-NiSn respectively at 498 K	Comparable performance with platinum-based catalysts for production of hydrogen from ethylene glycol, glycerol, and sorbitol
Pt	Ni, Co	PtNi/Al ₂ O ₃ , PtCo/Al ₂ O ₃	2.8–5.2 at 483 K	2.1–3.5 times higher than Pt/Al ₂ O ₃
Pd	Fe	Pt ₁ Fe ₉ /Al ₂ O ₃	0.3–4.3 at 453 to 483 K	Three times higher than Pt/Al ₂ O ₃
	Fe	Pd ₁ Fe ₉ /Al ₂ O ₃	1.4 and 4.3 at 453 and 483 K respectively	39–46 times higher than Pd/Al ₂ O ₃ at the same reaction conditions.
		Pd/Fe ₂ O ₃	14.6, 39.1 and 60.1 at 453, 483 and 498 K respectively	higher intrinsic activity and TOF _{H₂}

turnover frequencies for hydrogen production (TOF_{H₂}) than monometallic Pt and Pd catalysts for APR of ethylene glycol. The authors commented that the alloy formation decreases the strength of interaction of CO and hydrogen with the catalyst surface which increases availability of the C–C scission active sites. They also attributed the higher TOF_{H₂} obtained in the bimetallic catalyst to enhancement of the activity of Pt due to alloying effects of the metals (Ni, Co and Fe).¹¹⁸ However, it appears that the observed catalytic performance is intrinsic to the metals (Ni, Co and Fe) and not Pt since the metals have higher C–C scission than Pt & Pd and ratios of the metals to Pt or Pd in the bimetallics is >1.

It is noteworthy that Pd/Fe₂O₃ (Table 7) displayed higher TOF_{H₂} than the Pt and Pd bimetallic catalysts. These catalysts are prepared by incipient wetness impregnation of the supports with metal precursors. The performance of Pd/Fe₂O₃ was attributed to synergy of C–C scission activity of Pd nanoparticle and WGS promoting effect of the support, Fe₂O₃. In another related report Liu *et al.*,¹¹⁹ showed that Pd/Fe₃O₄ catalyst exhibited intrinsic activity three times that of Pd/Fe₂O₃ catalyst for APR of ethylene glycol under the same reaction conditions. The Pd/Fe₃O₄ and Pd/Fe₂O₃ catalysts were prepared by co-precipitation and incipient wetness impregnation respectively. Co-precipitation method produced highly dispersed Pd nanoparticles and higher resistance to sintering than impregnation method. Again, performance of the Pd/Fe₃O₄ catalyst was attributed to enhanced synergistic effect of the small Pd nanoparticles and WGS promoting effect magnetite. Chu and associates¹²⁰ also reported APR of ethylene glycol over Co/ZnO catalysts prepared by co-precipitation method. They observed that at Co/Zn < 2 results in ZnO and ZnCo₂O₄ spinel as main phases. At Co/Zn slightly greater than 2, a small amount of Co₃O₄ appeared, but the reduced catalysts composed of highly dispersed Co and ZnO. The Co/ZnO catalysts were found to give higher hydrogen selectivities than RANEY® Ni catalyst at similar conversion.

Luo and co-workers¹²¹ investigated APR of glycerol over Ni–Co bimetallic catalysts. They explained that temperature programmed reduction (TPR) profiles of the Ni–Co bimetallic catalysts indicated synergism for APR of glycerol. The catalysts, prepared by urea matrix combustion method, suffer from deactivation due to deposition of carbon plagues. But inclusion of cerium in the compositions was found to suppress sintering and methane formation on the catalysts. Pt supported Fe–Cr mixed oxide catalysts has also been tested for APR of ethylene

glycol. The mixed oxide was prepared by combustion method using citric acid as fuel. It was shown that the presence of Cr in the mixed oxide support increased hydrogen productivity of the catalysts.¹²² Furthermore, it has also been indicated that γ -Al₂O₃, commonly employed as support because of its high metal dispersion, is susceptible to phase changes under APR conditions.¹²³ Alumina nanofibre and single-walled carbon nanotubes have been reported to display greater stability than γ -alumina under APR conditions.^{113,124} Calcium aluminate (12CaO·7Al₂O₃)-supported metal catalysts have been shown to display better hydrogen production activity than alumina in the steam reforming of bio-oil.¹²⁵ Since APR shares catalyst site requirements with SMR, 12CaO·7Al₂O₃ could be a better choice as metal support for hydrogen production activity in APR.

The above shows that there are wide options in the quest for non-precious metal APR catalysts. It underscores role of metal support and preparation method in the design of APR catalysts. Desired properties in supports for APR catalysts may include: WGS activity, basicity or stability in basic media and higher metal dispersion. The ability of the support to inhibit sintering of the metal nanoparticles and coke formation are also crucial to the efficiency of the APR catalysts. In addition, strategies used for improving catalyst life-span identified in internal reforming and current enhanced steam reforming can be explored in APR.

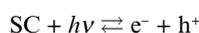
3.2 Photocatalytic reforming

The amount of heat and radiant energy from the sun that reaches the earth annually is far greater than the annual global energy consumption. But only a small fraction of it can be harvested through natural processes (*e.g.* photosynthesis). Harnessing the abundant solar energy has been a long-time goal in the quest for renewable energy for sustainable development. However, the diffuse nature, varied supply and distribution of solar radiation have limited most exploitation of solar energy to primitive applications.¹²⁶ In order to expand the spectrum of usage of solar energy to advance applications, it must be converted or stored in a form that can be readily made available on demand to end users. The main challenge for exploitation of solar energy has been the development of efficient physical devices or chemical systems that can capture and store the energy. Lewis and Nocera argued that the most attractive means to store solar energy is in the form of chemical bonds through the production of solar chemical fuels.¹²⁷ In line with the desire

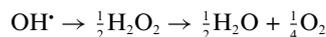
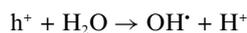
for a renewable route to hydrogen, a combination of renewable hydrogen substrates and solar radiation can be adjudged carbon free and sustainable. Hence, photocatalysis qualifies as a tool for storing solar radiation in the form of chemical bonds through hydrogen production from renewable hydrogen substrates (water and biomass).

Photocatalysis involves oxidation and/or mineralisation of a substrate by a semiconductor (SC) nanocrystal (photocatalyst), through a series of chain reactions. The most critical in the series of reactions is the initiation step, which is photoexcitation of electrons in the photocatalyst by absorption of a photon. This leads to generation of an electron–hole pair. The ‘electron’ and the ‘hole’ induce reductive and oxidative processes respectively.¹²⁸ For example, photocatalytic splitting of water into hydrogen and oxygen can be represented as follows:

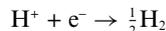
Photoexcitation:



Oxidation:



Reduction:



Holes generated in the semiconductor can oxidise organic species directly or indirectly in combination with OH^\cdot in aqueous solution. However, recombination of the electron-hole pair is a competing reverse reaction in the initiation step and can adversely affect the rate of the subsequent reactions. One of the strategies to inhibit the recombination is addition of sacrificial molecules (hole scavengers) that are more active than water at reacting irreversibly with the holes. When such molecules are added (dissolved) to water with the intention of sacrificing them for hydrogen production, the reaction is then referred to as ‘photocatalytic reforming’.¹²⁹ To this end, alcohols displayed particular abilities and alcohols from biomass are of special interest in order to make the process carbon-neutral. Photocatalytic reforming of methanol, ethanol, glycerol, glucose and acetic acid have been investigated. Generally, it was observed that addition of these renewable oxygenates remarkably enhanced the rate of hydrogen formation and the reaction kinetics followed the Langmuir–Hinshelwood model.^{130–132}

According to Juan and associates¹²⁹ an ideal photocatalyst should possess the following attributes: must be chemically and biologically inert; available at low cost; must adsorb the reactant under efficient photonic activation. TiO_2 is the only semiconductor that meets most of the listed criteria. Hence, it is the most investigated semiconductor for photocatalytic splitting of water or photocatalytic reforming. However, pure TiO_2 absorbs only ultraviolet light which is just four percent of the solar energy. A photocatalyst that is capable of absorbing visible light will be able to harness a greater portion of solar energy for the reaction. Different approaches are being explored to enhance the performance of TiO_2 . These include: doping (with metal, metal ion or anion) ion implantation, dye sensitisation, formation of composite semiconductors. These strategies have been reported to have a positive impact on the performance of

TiO_2 , particularly ion implantation and dye sensitisation have been indicated to be very effective at extending the spectrum of activity of TiO_2 from ultraviolet to visible light range. Conversely, ion-implanted and dye-sensitized TiO_2 suffers a stability problem.¹³¹ In addition to broadening the activity spectrum of TiO_2 , metal doping also inhibits recombination of the electron-hole pair. Precious metals, especially Pt, have a higher enhancement effect on TiO_2 photoactivity.^{132–134} Because of the high cost of the noble metals, cheap and readily available transition metals have been explored for metal doping of TiO_2 . Vanadium, copper, iron and zeolites have been indicated as promising. Intimate contact between the metal and TiO_2 is crucial to the performance and stability of the catalyst. Oxidising and acidic reaction environments promote leaching of the doped metals, thus, anaerobic and neutral pH conditions are generally preferred for photocatalytic reforming.^{135–139}

Photocatalytic reforming is relatively in the infancy stage, and at present most investigations on it are still largely on the laboratory scale. There is not yet a single report about any pilot studies on photocatalytic reforming towards commercial hydrogen production. Nevertheless, since the process is often carried out at room temperature and both the energy and feedstocks are from renewable sources, photocatalytic reforming can be said to be especially promising for sustainable large scale production of renewable hydrogen.

3.3 Solar reforming

The use of solar energy as the heat source to drive endothermic chemical reaction adds to avenues for harnessing the vast abundant renewable energy. A mix of solar heat and chemical raw material leading to chemical products constitutes solar chemical technology. This integration could be a bridge from the present fossil fuel-based commercial hydrogen production to commercial hydrogen production exclusively from renewable sources. The concept of solar chemical technology is not new, initiatives for its application in fuel processing dates back to the energy crisis of the 1970s. Commercial and research attention on it declined after the energy crisis ended.¹⁴⁰ However, there is a renewed interest in solar chemical technology for fuel processing as part of the quest toward a paradigm shift from fossil fuels to an economy based on renewable energy. Solar energy is the largest exploitable renewable energy resource. Its characteristics in its natural form renders it unsuitable as a heat source to drive highly endothermic chemical process. These characteristics must be modified or compensated for to make it suitable for application in highly endothermic chemical processing or fuel processing. When used to drive reforming reactions for hydrogen production, it is referred to as solar reforming. To this end, concentrated solar power (CSP) technologies provide modified solar heat sources that are suitable as energy input that can drive reforming reactions. Table 8 shows a list of different CSP technologies and their characteristics.

There have been a number of reports on the use of CSP technologies as renewable energy source for reforming methane.^{142–145} CSP as a renewable heat source when coupled with renewable hydrogen substrates will make hydrogen production through solar reforming exclusively from renewable sources. To date, methanol and ethanol are the only oxygenated hydrogen substrates that

Table 8 CSP technologies and their characteristics¹⁴¹

CSP technology	Classification	Flux power	T/°C
Parabolic Trough Collectors (PTC)	Low- and mid-end	30–80	400
Liner Fresnel Systems (LFS)	Low- and mid-end	30–80	400
Central Receivers System (CRS)	High-end	200–1000	>1000
Dish-Stirling Engine (DSE)	High-end	1000–4000	>1500

Classification is based on technology level technology application.

have been explored *via* solar steam reforming.^{146–147} Steam reforming of ethanol usually takes place at high temperature and may require advance CSP technologies (high end), which may be capital intensive. However, aqueous phase reforming (APR) is carried out at much lower temperature than steam reforming using low cost hydrogen substrates from renewable sources. Here, less capital-intensive low- and mid-end CSP technologies can readily suffice for APR. Thus, APR-CSP (low- and mid-end) couple could mark a new path to renewable hydrogen production technology with the potential of being competitive with the present commercial SMR technology.

4 Conclusion

Today global climate change is a worldwide environmental concern, and global warming is closely linked with greenhouse effect of CO₂ emission. Although hydrogen has been focused as an environment friendly energy carrier to replace the present hydrocarbon carriers from fossil fuels, the chances of adoption of hydrogen as a universal energy carrier in the near future appear slim. While hydrogen consumption for traditional applications is on the increase, the hydrogen demands of these traditional uses are still being met from non-renewable resources. A sizeable reduction in CO₂ emission cannot be achieved by more efficient use of fossil fuels energy alone. To enable sustainable growth, the need for commercially viable technologies for production renewable energy cannot be over emphasised. A truly renewable hydrogen need to be produce from renewable inputs. Plants through photosynthesis use solar energy to produce biomass. The same solar energy is in excess that can be exploited to process biomass into hydrogen and other fuels. As part of the preparedness towards gradual transition from non-renewable to renewable energy sources, it is imperative to encourage the entry of reforming technologies for hydrogen production from biomass and solar energy into the hydrogen market. To this end, APR-CSP couple, photocatalytic and solar reforming of renewable oxygenates are identified as promising reforming technologies for hydrogen production exclusively from renewable resources.

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