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Hydrogen via steam reforming of liquid bio-feedstock

Gaurav Nahar* and Valerie Dupont

Energy Research Institute, School of Process, Environmental and Materials Engineering, The University of Leeds, LS2 9JT, UK

g.nahar05@leeds.ac.uk, V.Dupont@leeds.ac.uk

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Summary:

This review paper examines the use of steam reforming to convert bio-liquids like ethanol, glycerol, butanol, vegetable oil, bio-oils and biodiesel into hydrogen gas. The focus of the research was to investigate the research being undertaken in terms of catalyst developments for the steam reforming of the above mentioned feedstock, and to determine the perspective opportunities in this area. Hydrogen production by steam reforming of bio-oil, ethanol, and pure glycerol has been widely investigated; several thermodynamic and catalytic investigations are available restricting new investigations. In contrast, hydrogen production from waste streams, vegetable oil, biodiesel and butanol is very recent and has room for further developments.

1. Introduction:

Fuel cells are considered as one of the cleaner energy conversion devices for the future. Proton exchange membrane fuel cells (PEMFC) are considered as a promising option for mobile auxiliary power units (APU) for transportation applications, while solid oxide fuel cells (SOFCs) are considered mainly for stationary combined heat and power (CHPs) [1, 2]. PEMFC require high purity hydrogen, whereas SOFCs can operate on H_2-rich syngas. Hydrogen does not exist freely in nature, but it can be obtained from fossil fuels, biomass, or water. On a global scale, approximately 40 million tons of hydrogen gas are produced annually, but most of it is used in ammonia production for fertilizers, oil refining, and methanol synthesis [3]. Carbonaceous raw material, principally fossil fuels account for 95% of the hydrogen produced today by steam reforming (SR) or steam gasification.

In order to supply greener hydrogen from steam reforming, it is necessary to use renewable gaseous or liquid fuels. High energy density liquid fuels can be stored and transported safely. These can be converted to a hydrogen rich gas (reformate) via fuel processor for delivering the hydrogen for the fuel cells based APUs and CHPs [4, 5]. The objective of this paper is to examine the use of catalysts for the production of hydrogen from liquid feedstock of biomass origin like ethanol, glycerol, bio-oil, butanol, vegetable oil and biodiesel for fuel cell applications. Although methanol and dimethyl ether as a hydrogen carrier for fuel cells have been evaluated in several investigations [6, 7], these can be directly used in fuel cells [8] rather than reforming them, further the hydrogen produced from methanol is lower as compared to ethanol over other alcohols like butanol or glycerol, hence were not selected for this review.

In the fuel processing system which precedes the fuel cell, the most important part is the fuel reformer, which converts the fuels, i.e. biomass-derived feedstock, into hydrogen rich gas. Figure 1 represents a schematic of a fuel processor to be used for APUs. A vaporizer is always necessary to preheat the fuel, steam, and air before they are fed to the reformer. The reformer could be based on steam reforming (SR), partial oxidation (PO), or autothermal reforming (ATR). As compared to ATR and PO, SR is the most developed and most used technology. The thermal efficiencies based on the higher heating values is about 70-80% for SR in comparison to 60-75 % for both ATR and PO respectively, making it suitable for generating hydrogen from bio-liquid feedstock [9]. Although PO has similar thermal efficiency as ATR, oxidation of liquid hydrocarbons is easier as compared with gaseous ones resulting in lower hydrogen yield. Lower conversion and selectivity to hydrogen is reported in PO of alcohols like methanol on monometallic catalyst making it less desirable [10]. Given that biofuels usually contain higher or equal carbon than oxygen on a molar basis, the reactions below illustrate the higher yield in hydrogen achieved by SR compared to PO. They also show how the oxygen content of the fuel causes a hydrogen yield penalty for SR, but make PO more economical by requiring less oxygen co-reactant.

$$\text{Steam Reforming }(\text{SR}):\ \mathrm{C}_n\mathrm{H}_m\mathrm{O}_k + (n-k)\ \mathrm{H_2O} \xrightleftharpoons{\Delta\mathrm{H}>>0} n\mathrm{CO} + (n+0.5m-\mathrm{k})\ \mathrm{H}_2 \tag{1}$$

$$\text{Partial Oxidation }(\text{PO}):\ \mathrm{C}_n\mathrm{H}_m\mathrm{O}_k + 0.5(n-k)\mathrm{O}_2 \xrightleftharpoons{\Delta\mathrm{H}<0} n\mathrm{CO} + 0.5m\mathrm{H}_2 \tag{2}$$

The hydrogen rich gas produced from the reforming process becomes the feed to high and low temperature water gas shift reactors in series to remove CO. A final purification step by adsorption of the non-hydrogen by-products, or of CO_2 removal steps (e.g. by methanation) follow if necessary.

$$\text{Water Gas Shift }(\text{WGS}): n\times(\mathrm{CO} + \mathrm{H_2O} \xrightleftharpoons{\Delta\mathrm{H}<0} \mathrm{CO_2} + \mathrm{H_2}) \tag{3}$$

$$\text{Methanation }(MTH): n(CO+3H_2 \xrightleftharpoons{\Delta\mathrm{H}<0} CH_4+H_2O) \tag{4}$$

Most industrial steam reformers use Ni catalysts on a ceramic support, operating in the temperatures ranging from 973-1223 K in the pressure range of 15-30 atm [11, 12]. The high temperatures thermodynamically favour the SR reactions as opposed to high pressures. In industry the high pressure operation is made necessary due economies of scale. Since first developed in 1926, for several decades SR has been used for hydrogen production from natural gas via syngas[12]. As CH_4 is a very stable molecule, severe temperatures are required, e.g. over 800 ^oC, for converting methane to H_2, CO, CO_2 and H_2O. The reaction is performed in costly tubular reactors of high Ni-content called reformers, packed with Ni based catalyst pellets, and under steam/methane molar ratios between 2.5 and 5. Alkali metals and excess of steam are used in the catalyst to promote coke removal. The SR reaction is strongly endothermic, and reactor designs are typically limited by heat transfer from the burners through the reformer tubes and inside the pellets, rather than by reaction kinetics [4]. In comparison to methane, liquid fuels are easy to reform because they dissociate at lower temperatures, however their hydrogen yield is lower according to the stoichiometry of the SR reaction, and to the equilibrium of the methanation reaction. The most significant advantage of SR is the highest hydrogen yield in comparison to other processes, by extracting the hydrogen of both the fuel and the water co-reactants, making it the most desirable.

According to the reactions above, the maximum theoretical hydrogen yield via combined SR and WGS -notwithstanding thermodynamic limitations- is ($2n+0.5m-k$) mol H_2 per mol of ($C_nH_mO_k$) feedstock, compared to ($n+0.5m$) for combined PO and WGS. The yield is most commonly reported in the literature in mol H_2/mol fuel, wt% of the fuel, and sometimes as a percent of the theoretical maximum yield, where the maximum is either from the complete SR and WGS reactions. When the yield is given as a % of a maximum, a more appropriate term ought to be ‘yield efficiency’. The less common definition of hydrogen yield on the basis of both fuel and water co-reactant (molar or mass basis) may be used specifically for mobile applications, where both reactants require transport and incur an energy cost. In some cases reporting experimental results, the yield can also be reported as a percent of the maximum yield predicted by thermodynamic equilibrium, when known. This allows comparison between catalysts based to their ability to bring the reactive system closer to thermodynamic equilibrium, evidencing faster reaction kinetics.

The maximum percent purity of H_2 in the products mix is then $100\times(2n+0.5m-k)/(3n+0.5m-k)$ for combined SR and WGS, compared to $100\times(n+0.5m)/(2n+0.5m)$ for combined PO and WGS. For e.g. the maximum hydrogen yield from complete steam methane reforming and water gas shift notwithstanding equilibrium considerations is 4 mol/mol of CH_4 (or 50 wt% of CH_4) with a maximum purity of 80 vol%, compared to 3 mol/mol (or 37.5 wt%), with a maximum hydrogen purity of 75 vol% (EQ-25) using methane partial oxidation and water gas shift.

Performance of the combined SR-WGS process is also reported in terms of selectivity to hydrogen, whose correct definition ought to be the ratio of the molar production rate of hydrogen to the sum of the molar production rates of all the hydrogen containing products (e.g. H_2, CH_4, C_2H_6, C_2H_2, NH_3), where purity is defined by EQ-25.

In the literature, the terms yield and selectivity are often misused for concentrations, mol fractions and purity, and readers need to exert caution accordingly when comparing the process performance indicators from different publications. These definitions are provided in the abbreviation and nomenclature section.

2. Ethanol steam reforming:

Use of ethanol as an alternative fuel has been widely examined. Ethanol (C_2H_5OH), is used for blending with gasoline, with 10 and 22 vol% blends commonplace in the US and Brazil, respectively [13]. It is an oxygenated fuel that contains 35 wt% oxygen, which reduces particulate and NOx emission from combustion [14]. It has a number of environment benefits, due to low pressure and reduced emission along with clean burning characteristics [15]. Steam reforming of ethanol ('SRE') has been widely investigated through thermodynamic simulations and catalytic experiments. According to the stoichiometry of the reactions, corresponding to a steam to ethanol molar ratio ('S/EtOH') of 3, the maximum theoretical yield of hydrogen from SRE followed by WGS (notwithstanding equilibrium limitations) is 6 mol H_2 per mol of ethanol, equivalent to 26 wt% of ethanol, with a maximum hydrogen purity of 75 vol% before separation of CO_2.

2.1 Thermodynamic investigations:

Wang and Wang [16] calculated a 60.52– 83.58% hydrogen yield (EQ-5) with 32.82–79.60% carbon monoxide yield at steam to S/EtOH between 3-6 at 900–1200 K in thermodynamic analysis of SRE. The authors reported that, as expected from Le Chatelier's principle, increase in pressure restrained hydrogen formation as a result of shift in the equilibrium to reactants in the SR reactions. Further increase in pressure was reported to increase coke selectivity. Figure 2a presents the H_2 yield (in wt% of fuel) from SRE at thermodynamic equilibrium as function of temperature for S/EtOH values ranging from lack of steam to excess of steam. It exhibits the trend of increasing hydrogen yield with increasing steam to fuel ratio following Le Chatelier's principle, and the shift towards lower temperatures for the peak hydrogen yield as the steam to fuel ratio increases (effect of disparity in the reaction enthalpy between the endothermic SR and the mildly exothermic WGS). These trends are typical of steam reforming of any oxygenated and non oxygenated fuels, whereby a range of temperatures for optimum hydrogen yield can be identified, and the choice of steam to fuel ratio for a practical operation is guided by the cost of raising steam and the availability of distilled water. Alvarado and Gracia [17] predicted carbon deposits i.e. graphite, nanotubes and amorphous in SRE with respect to S/EtOH. Formations of various carbons were reported below S/EtOH of 4. Below 673 K graphite dominated, while above 673 K nanotubes took over carbon formation. The formation of amorphous carbon was absent in the equilibrium evaluations. Likewise Silva et al. [18] reported detailed thermodynamic predictions of carbon species formation during SRE. The effect of contact times on carbon formation was examined in detail. Lower contact times favored the formation of carbon. At lower contact times, the S/EtOH had no effect on carbon formation, while at higher contact times S/EtOH greatly influenced carbon formation. At lower contact times, formation of ethylene and acetaldehyde were reported to be the reason for carbon formation.

Catalysts play a crucial role in the reactivity toward complete conversion of a liquid fuel. However, each catalyst may induce a different pathway, and therefore, the selection of a suitable catalyst plays a key role in SR for hydrogen production. Active catalysts should maximize hydrogen selectivity and inhibit coke formation as well as CO production. Development of a highly efficient, stable, and coke resistant catalyst has been undertaken by several researchers. Monometallic, bimetallic, single and mixed oxide supports have been evaluated. This section discusses the performances of various catalytic systems (single or combined metals and single or mixed oxide supports) in SRE.

2.2 Catalytic investigations:

Bshish et al. [19] reviewed the various catalyst used in SRE. The authors examined the use of various noble and non noble metal based catalyst for SRE. Similarly the uses of various supports on the performance of the catalyst were also examined. Ni, Cu and Rh were reported to be the most suitable metals for the hydrogen production by SRE. Ni and Cu would be preferred over the precious metal Rh for economic reasons. Mixed oxide supported metal catalysts were reported to be promising catalyst for future investigations, due to maximum conversion and hydrogen yield. Likewise Meng et al. [20] reported that Rh and Ni metals exhibited the best performance in terms of conversion and hydrogen selectivity in SR of bio-ethanol, while MgO, ZnO, CeO_2, and La_2O_3 could be used as supports due to their ability to reduce coke formation. Development of double-bed reactor, bi-metallic catalyst, and alloy catalyst were reported to be promising in achieving high hydrogen production and low carbon deposition. Table 1 summarizes the results of various investigations in terms of hydrogen yield, selectivity and molar composition in the SRE.

Table 1: Investigations in terms of hydrogen yield, selectivity and molar composition for SRE.

Over decades Ni based catalyst have been widely used as SR catalyst. These catalysts are relatively inexpensive and the spent catalyst can be recycled and reused. Nickel supported on various supports for SRE has been widely investigated by several research groups. Alberton et al. [21] studied SRE over Ni supported Al_2O_3 catalyst at 873 K and S/EtOH of 3. The effect of type of Al_2O_3 on the SRE was examined. Catalyst supported on α-Al_2O_3 showed lower catalytic activity in comparison with γ-Al_2O_3 due to lower dispersion of Ni particles. Formation of large amounts of encapsulating coke, as result of ethylene formation via dehydration of ethanol on γ-Al_2O_3 was reported as the reason for deactivation. It is well known that the presence of acidic sites on this catalyst surface promotes coke formation by polymerization processes of CH_x species formed during SR. Encapsulating coke covers the surface of the active metal of catalyst resulting in deactivation. In comparison, α-Al_2O_3 was reported to deactivate as result of Boudouard or methane decomposition reaction. The activity of the α-Al_2O_3 supported catalyst was reported to increase due to activation with a methane/oxygen mixture as result of migration of Ni particles on carbon filaments. The strong interaction between Ni species with the support made γ-Al_2O_3 supported catalyst hard to reduce by methane/oxygen mixture. The authors reported that dispersion of Ni on α-Al_2O_3 was lower as compared to γ-Al_2O_3 and hence increasing loading had no significant effect on the activity of the Ni/α-Al_2O_3 catalyst. On the other hand 8 and 16% Ni on γ-Al_2O_3 catalysts showed similar performance.

At higher temperature i.e. 1023 K and S/EtOH of 3, Fatsikostas et al. [22] found that Ni supported on La_2O_3 exhibited higher catalytic activity in comparison to Al_2O_3, YSZ and MgO supported Ni catalyst. But at 873 K, a La_2O_3 supported catalyst formed undesirable CH_3CHO and CH_4, thus lowering hydrogen selectivity. They also investigated the use of Ni supported on La_2O_3 modified Al_2O_3 catalyst for SRE, formation of ethylene below 873 K was reported as a result of Al_2O_3 addition. Higher temperature i.e. 1073 K was required for the complete conversion of ethanol and higher hydrogen selectivity over this catalyst. In contrast to Alberton et al.[21], Sun et al. [23] showed that Ni/Al_2O_3 had lower catalytic activity in low temperature SRE. However Ni supported Y_2O_3 and La_2O_3 exhibited high catalytic for low temperature (590 K) SRE with same S/EtOH of 3. The catalytic activity followed the order Ni/La_2O_3>Ni/Y_2O_3>Ni/Al_2O_3. Highest conversion and selectivity was recorded at 590 K. All the catalysts examined exhibited long term stability for SRE. Sánchez-Sánchez et al. [24] reported that addition of La_2O_3 modified the acidity of γ-Al_2O_3 reducing the formation of ethylene responsible for coke formation in SRE. Ni supported on La–Al_2O_3 exhibited a closer interaction between the La and Ni phases. At higher La loading, La entities were present on the top of metallic Ni crystallites. The close contact between Ni and La atoms may have increased the blocking of Ni sites reactive to ethylene dehydrogenation to coke. Similarly authors reported that Ni supported on MgO–Al_2O_3 exhibited better catalytic activity in comparison to Ni/Al_2O_3. Addition of MgO decreased the surface acidity of Al_2O_3 and modified the interaction degree of Ni with Al_2O_3 by intercalation of the promoter between Ni and Al_2O_3. The latter was found to inhibit the incorporation of Ni to Al_2O_3 phase, improving the Ni dispersion [25]. Sorption enhanced SRE was carried out by He et al.[26] in order to produce high purity hydrogen using Co−Ni catalysts derived from hydrotalcite (HT) like material at S/EtOH of 6 and temperatures ranging from 823 to 923 K. They reported that 40Ni and 20Ni-20Co/ HT catalyst at 823 K yielded the best results, with 99 mol % hydrogen purity (EQ-25) and just 0.1 mol % carbon monoxide. Further the authors also reported the effect of steam on the stability of the CO_2 sorbent during the sorption enhanced SRE reaction. Hydration of calcium oxide in the sorbent did not cause appreciable induction period, even at the low operating temperatures, while under dry conditions the sorbent showed rapid deactivation in multiple cycles. Figure 3 represents the performance of 40Ni/HT catalyst in sorption enhanced SRE at 823 K with S/EtOH of 6 at 1 atm [26].

CeO_2 based materials have received lot of attention in SRE. A high oxygen mobility (redox property), high oxygen storage capacity, strong interaction with the supported metal (strong metal–support interaction) and their ease of modification promoted several investigations of hydrogen production by SRE over CeO_2 supported catalysts [27-29]. Fajardo et al. [30] performed SRE with S/EtOH of 3 at 673 K over Ni supported over CeO_2 catalyst prepared by using a biopolymer polymerization method. They showed that formation of ethylene due to dehydration reaction was absent over this catalyst, unlike that prepared by conventional impregnation of commercial CeO_2. All the ethanol was converted at the conditions examined, and acetaldehyde was seen as an intermediate product obtained by dehydrogenation of ethanol. Laosiripojana and Assabumrungrat [31] showed that Ni supported on CeO_2 prepared by a surfactant assisted method exhibited higher resistance to coke formation in comparison to Ni/Al_2O_3 and CeO_2 by precipitation method. Formations of C_2H_4 and C_2H_6 compounds were reported responsible for catalyst deactivation of Al_2O_3 and precipitated the CeO_2 catalyst. The experiments were performed at S/EtOH of 3 and 1173 K.

One of the major limitations of ceria is deactivation due to sintering rate at high temperatures [32, 33]. It also has very low surface area. When exposed to high temperatures the specific surface area of CeO_2 decreases drastically which in turn lowers its redox properties and oxygen storage/release capacity [34]. The oxygen transfer capacity of ceria in catalytic reactions is considered as a means to prevent deactivation by coking. Studies have shown that addition of ZrO_2 into CeO_2, improves the redox property, oxygen storage capacity and thermal stability, resulting in better performance in CO oxidation and methane combustion. Hence several investigations of SRE over Ni supported on Ce-ZrO_2 catalyst have been performed [35, 36]. Like CeO_2 Ce-ZrO_2 supported catalysts are more active in SR reactions in comparison to ethanol dehydration reaction in SRE [37]. Biswas and Kunzru examined SRE over $Ni/Ce_{1-x}Zr_xO_2$ (x=0, 0.26, 0.59, 0.84 and 1) catalyst prepared by co-precipitation method [36]. $Ni/Ce_{0.74}Zr_{0.26}O_2$ catalyst with 30 wt% metal loading exhibited high catalytic activity and hydrogen selectivity (5.8 mol/mol of ethanol) at S/EtOH of 8 and 873 K. High activity of 30 wt% $Ni/Ce_{0.74}Zr_{0.26}O_2$ was reported due to high oxygen storage capacity of cubic $Ce_{0.74}Zr_{0.26}O_2$. Ni supported $Ce_{0.74}Zr_{0.26}O_2$ catalyst also showed higher selectivity in comparison to Ni supported CeO_2. Considerable amount of side products (C_2H_4, C_2H_6, CH_3CHO and CH_3COCH_3) were obtained on a Ni supported CeO_2 catalyst. While Srinivas et al. reported that 40 wt% Ni catalyst exhibited higher catalytic activity over $Ce_{0.3}Zr_{0.5}O_2$ prepared hydrothermally using a rotating autoclave in SR of bioethanol. The catalyst was stable for more than 500 h containing 5 ppm S [35]. In comparison to Ni/ γ-Al_2O_3 examined by Alberton et al.[21], Ni loading showed a significant effect on $Ce_{0.74}Zr_{0.26}O_2$ supported catalyst. Authors reported that hydrogen selectivity was lower at all the metal loading below 773 K, while hydrogen selectivity increased with metal loading over 823 K with 30 and 40 wt% exhibiting comparable selectivity.

Among all the catalyst examined by different authors summarized in Table 1, highest activity was obtained on 30 % Ni supported on $Ce_{0.74}Zr_{0.26}O_2$ with lower production of by-products like CO and CH_4[36]. The high activity of this catalyst was attributed to high Ni loading and the reduction behavior of the catalyst. The reduction behavior was strongly dependent on the support and high activity was related to the degree of reduction of nickel, making higher amount of reduced nickel available for the reaction. Similarly the formation of by products like acetaldehyde, acetone was lower over this catalyst, with zero selectivity to aldehyde reported above 823 K. The by-products are responsible for the formation of undesirable methane. The formation of alkenes like ethylene was less compared to Al_2O_3

based catalyst. The acidic sites on alumina have a tendency to dehydrate the ethanol leading to the formation of alkenes resulting in the coking of the catalyst. The presence of Zr in stabilizes the ceria lattice improving its thermal stability, redox property and oxygen storage capacity leading to better performance as mentioned before.

Ni on La_2O_3 also showed good performance with 100% ethanol conversion but at higher temperature i.e. 1023 K. The activity of the catalyst was attributed to its ability to scavenge coke deposition on the Ni surface by lanthanum oxycarbonate species which exists on top of the Ni particles under reaction conditions. But the catalyst did not exhibit good stability [30].

3. Steam reforming of glycerol:

Increased biodiesel production has resulted in greater availability of glycerol ($C_3H_5(OH)_3$), which is also termed ‘glycerin’. The principal by–product of biodiesel production is the crude glycerol, which is about 10 % wt of vegetable oil [38]. For a current biodiesel production of 150 million gallons/year, the glycerol amount is 50 million kg. High purity glycerol is a very important industrial feedstock. Its applications are found in food, drug, cosmetic and tobacco industries. In the past decade, the industrial price of glycerol was in the range of \$1.28 to \$1.65 [39]. Glycerol markets are limited; an increase in biodiesel production may cause glycerol prices to decline from \$1/L to \$0.7/L by 2010 [40].The cost of purifying the glycerol is also high [41]. Thus efforts on utilization of this abundant and cheap resource for the production of hydrogen or synthesis gas have been increasingly appearing in the literature [42]. Several investigations on thermodynamic and catalytic investigations on the steam reforming of glycerol (SRG) have been reported [43-50]. Table 2 lists the outcomes of various investigations in terms of hydrogen yield, selectivity and molar composition in the SRG. Before equilibrium limitations, the theoretical maximum yield of hydrogen from SRG followed by WGS is 7 mol of H_2 per mol of glycerol or 15.2 wt%, which occurs at a steam to glycerol molar ratio (S/G) of 3. The maximum H_2 purity is then 70 vol%.

Table 2: Investigations in terms of hydrogen yield, selectivity and molar composition for SRG.

3.1 Thermodynamic investigations

The H_2 yield (wt% of fuel) from SRG calculated at thermodynamic equilibrium (Gibbs free energy minimization method, this work) and atmospheric pressure is shown in Figure 2b as a function of temperature for the molar steam to carbon ratio of 3, alongside that of the other biofuels considered in this review. It is situated significantly below that of ethanol due to its higher oxygen to carbon ratio.

Adhikari et al. [43] carried out a thermodynamic evaluation of SRG using the Gibbs free energy minimization method. They found the best conditions for producing hydrogen were at a temperature >900 K, with S/G of 9, and a pressure of 1 atm. A hydrogen yield of 6 mol/mol of glycerol (i.e. 85.71 % by EQ-6) at 960 K was measured at these conditions. Slightly lower optimal temperature for production of hydrogen in thermodynamics SRG was reported by Chen et al. [44]. Optimal conditions for hydrogen production (6.2 mol/mol of glycerol i.e. yield of 88.57 % by EQ-6) was reported at 853 K with steam to glycerol molar ratio (S/G) of 9, and a pressure of 1 atm. The authors also reported the effect of pressure and N_2 dilution on the process. With increasing pressure, molar productions of hydrogen and carbon dioxide decreased, whereas that of methane increased. Increasing N_2 dilution had the opposite effect from increasing pressure, as the introduction of an inert decreased the partial pressure of the products. The effect of pressure on the carbon monoxide production was negligible. In contrast to Adhikari et al. [43] and Chen et al. [44], a higher S/G was reported by Cui et al. [45] required to achieve highest hydrogen production in thermodynamic evaluation of SRG. They found the highest hydrogen yield i.e. 6.33 mol/mol of glycerol (90.48% by EQ-6) at 903 K at S/G of 15 and a pressure of 1 atm.

Authayanun et al. [46] reported different thermodynamic reformer operation conditions for generating hydrogen depending on the type of fuel cells utilizing the hydrogen produced. For low temperature PEMFC, the optimal conditions for the SRG process integrated with a water gas shift reactor (WGS) reactor was reported to be 1000 K with S/G of 6 and WGS reactor operating at 473 K. In case of high temperature PEMFC higher S/G of 12 was required at same conditions. Considering the performance of the glycerol steam reformer in terms of energy efficiency, the operation of the reformer at S/G of 11–14 produced the highest reformer efficiency when reformate gas contained 5% CO was considered. Approximately 6 of hydrogen mol/mol of glycerol was obtained under the conditions for low temperature PEMFC and high temperature PEMFC operated with 5% CO in the reformate gas.

3.2 Catalytic investigations:

Adhikari et al. [47] investigated the effect of catalyst support in SRG with S/G between 6 to 12 and the temperature range 823-923 K with varying feed flow from 0.15 to 0.45 ml/min. They reported Ni/CeO_2 as the best catalyst in SRG as compared to Ni/MgO and Ni/TiO_2. Ni/CeO_2 showed the highest surface area with the highest metal dispersion. Complete conversion on Ni/CeO_2 and Ni/MgO at all temperatures investigated in the study while Ni/TiO_2 showed the least conversion. Ni/CeO_2 yielded the maximum hydrogen selectivity (EQ-9) of 74.7 % at S/G of 12 and 873 K. The authors also investigated SRG over noble metals supported on coated Al_2O_3 monoliths [48]. A 2.5 wt% Ni/Al_2O_3 and $Rh/CeO_2/Al_2O_3$ with 2.5% ceria catalysts were found to exhibit the best performance in terms of hydrogen selectivity and glycerol conversion. Highest hydrogen selectivity of 80 %(EQ-

9) was obtained over Ni/Al_2O_3 at S/G of 9, 1173K and flow of 0.5 ml/min. While glycerol conversion was highest on $Rh/CeO_2/Al_2O_3$ catalyst as compared with Ni/Al_2O_3 at same S/G, temperature and feed flow rate. The decrease in feed flowrate was reported to increase glycerol conversion over $Rh/CeO_2/Al_2O_3$ catalyst while it decreased on Ni/Al_2O_3. Hydrogen selectivity increased slightly over $Rh/CeO_2/Al_2O_3$ but it decreased over Ni/Al_2O_3 catalyst. At same temperature i.e. 1173 K and S/G of 6 the order of hydrogen selectivity exhibited by the metals was Ni > Ir > Ru > Pt > Rh, Pd. With introduction of CeO_2 with Al_2O_3 selectivity of all the catalyst was higher compared to Al_2O_3 supported catalyst.

Buffoni et al. [49] reported that addition of CeO_2 to Al_2O_3 inhibited side reactions like dehydration, rearrangement and condensation reactions of glycerol, that lead to intermediate compounds responsible for coke formation in SRG. They compared the addition of 5 wt% ZrO_2 and CeO_2 to Al_2O_3 over 2 wt% Ni based catalyst in SRG with S/G of 9. At temperatures below 723 K, the capacity of Ni to break C–C bonds in glycerol was lower, allowing that dehydrogenated intermediates formed to suffer dehydration, rearrangement and condensation reactions. Activity and selectivity of Ni based catalyst was strongly dependent on the reaction temperature, with glycerol conversion to gaseous products. The minimum temperature of 823 K was reported to be required to obtain high hydrogen selectivity.

Chen et al. [44] performed SRG over CRG-LHR JM catalysts containing Ni (metal), NiO, Cr_2O_3, MgO and amorphous silica. SRG was performed in the temperature range 673-873 K, with S/G of 9 and reactant/inert gas of 1/4. The highest hydrogen yield of 88.57 % (EQ-6) with glycerol conversion over >96% were reported at ~853 K at the above conditions. Hydrogen selectivity was shown to increase with temperature; reaching 100 % at ~853 K. Increases in pressure were shown to adversely affect hydrogen yield and selectivity as a result of enhanced methanation of carbon monoxide. But increased pressure slightly affected glycerol conversion. Increases in S/G were shown to have positive effect on hydrogen yield and selectivity, while increases in reactant/inert decreased hydrogen yield and selectivity and enhanced methane formation. Growing residence times were reported to augment hydrogen production.

The process of sorption enhanced steam reforming has been investigated with pure glycerol and crude glycerol as the feedstock. In this process, a CO_2 sorbent is introduced within the reformer to modify equilibrium conditions through the in situ removal of the CO_2 gas, resulting in higher hydrogen yields and purity. Dou et al.[51, 52] reported complete conversion and 68 % hydrogen purity for crude glycerol in comparison with 65 vol% for pure glycerol at 873 K over 18% NiO/Al_2O_3 catalyst with S/G of 9 in SRG without carbon dioxide removal. Species concentrations with time on stream during steam reforming of crude glycerol with in-situ CO_2 capture are shown in Figure 4, leading to sorption enhancement. The period of pure hydrogen production is clearly visible in the first 1200 s, after which CO_2 breakthrough occurs and the hydrogen purity decreases gradually, indicating sorbent saturation.

In presence of the CO_2-sorbent dolomite the hydrogen purity increased to 90 and 94 vol% for crude and pure glycerol respectively through the effects of CO_2 in-situ capture [44]. Likewise complete conversion and higher hydrogen purity of 99 % (EQ-25) with S/G of 9 at 848 K with 25%-Ni-15%-Co/ HT type catalyst was reported by He et al [53].

In comparison to Adhikari et al. [47], Zhang et al. [50] reported complete conversion of glycerol at lower temperatures over Ir/CeO_2 catalyst, with S/G of 9 in the temperature range of 523-873 K. Glycerol was completely converted at 673 K over Ir/CeO_2 while complete conversion occurred at 698 and 723 K over Co/CeO_2 and Ni/CeO_2 catalyst respectively. Highest hydrogen selectivity of ~94.1% was reported at 823 K over Ir/CeO_2 catalyst, while Ni/CeO_2 showed the lowest at all the temperatures. The superior catalytic performance of the Ir/CeO_2 catalyst was reported as result of intimate contact between Ir particles and CeO_2 based on ceria-mediated redox process. Ir/CeO_2 and Ni/CeO_2 were reported to have better methane steam reforming and water gas shift activity in comparison with Co/CeO_2.

Iriondo et al. [54] reported lower catalytic stability for Ni/CeO_2 prepared by urea hydrolysis with very high S/G of 45, as compared with that obtained on commercial nanoscale CeO_2 reported by Adhikari et al. [47] with S/G of 9. The authors performed SRG under a (WHSV) of 7.7 h^{-1}, total pressure of 4 atm and temperatures between 773 and 873 K. Serious deactivation was reported after 2 h on stream at 773 K. The authors reported that temperature had no effect on the conversion of glycerol after 8 hours on reaction. The catalyst prepared by Iriondo et al. [54] had very low surface area as compared to that reported by Adhikari et al. [47] resulting in lower Ni dispersion and lower Ni loading on CeO_2. This was reported as the probable reason for lower catalytic activity rather than reduced activity as a result coke deposition. But similarly to Buffoni et al. [49] addition of CeO_2 to Al_2O_3 was reported to be beneficial for SRG. A 13 wt% Ni supported on 5 wt% CeO_2 doped γ-Al_2O_3 exhibited highest hydrogen yield and selectivity. The good activity of the catalyst was attributed to its ability to promote the formation of oxygenated hydrocarbons intermediates in SRG. Another explanation was its ability to the stabilize Ni° particles favored by the additional formation of Ni–CeO_2 species with higher interaction.

Dave and Pant [55] reported that ZrO_2 promotion of CeO_2 on Ni based catalyst results in higher hydrogen yield than that obtained with Ni/CeO_2 catalyst. They performed SRG with WHSV of 10.2 h^{-1} and S/G of 45 at 973 K. Addition of ZrO_2 suppressed the formation of methane and completely converted glycerol. Incorporation of ZrO_2 was shown to increase CeO_2 crystallinity and hence resulted in better Ni dispersion and subsequently good stability in comparison to Ni/CeO_2. Higher temperature, higher space time and lower glycerol feed concentration were shown to increase hydrogen yield and glycerol conversion. A 15 wt% Ni supported on 10 wt% ZrO_2 doped CeO_2 was shown to exhibit good performance with hydrogen yield of 3.95 (EQ-7).

In conclusion, Ir, Rh and Ni supported over CeO_2 and CeO_2 doped Al_2O_3 respectively have shown to be effective catalyst for SRG. Similarly to SRE, Ni supported on ZrO_2 promoted CeO_2 also showed promise for SRG as result of all the reasons and advantages explained in the previous section. For economic reasons, Ni based catalysts would be preferred over noble metals. Most catalytic evaluations are based on the use of pure glycerol rather than by-product glycerol, which contain impurities like soap, unreacted triglycerides, methanol and salts [56]. The performance of these catalysts would be affected as a result of the impurities in crude glycerol and there is significant room for further investigations on these effects.

4. Steam reforming of butanol:

Recently n-butanol has been proposed as an alternative to conventional gasoline and diesel fuels [57-60]. Butanol (C_4H_9OH) has the following advantages over ethanol [61]. It has a lower vapour pressure compared to ethanol and gasoline, which reduces the chance of vapour lock. It is less hygroscopic hence has enhanced tolerance to water contamination. It can be blended at higher concentrations directly with gasoline and diesel without retrofitting vehicles. It can be used in existing fuel distribution pipelines compared to ethanol. It has a higher heating value that is closer to that of gasoline (31.2 MJ/kg for butanol vs. 24.7 MJ/kg for ethanol; gasoline contains about 35.3 MJ/kg). The maximum theoretical hydrogen yield using SR is 12 mol of H_2/mol butanol, which is equivalent to 32.4 wt% of butanol. The maximum theoretical hydrogen purity from steam reforming of butanol (SRB+WGS) is 75 vol%. The stoichiometric steam to butanol molar ratio (S/BtOH) is 7 for combined SR and WGS.

BP and DuPont announced that they would start selling *n*-butanol, which they call 'biobutanol', as a gasoline blending component in the UK [62]. The above mentioned advantages and higher hydrogen content has prompted hydrogen production investigations from butanol.

4.1 Thermodynamic investigations:

Nahar and Madhani [63] examined the thermodynamics of steam reforming of butanol (SRB) for hydrogen production using a Gibbs free energy minimization method, with S/BtOH between 1 and 18 and pressure range of 1 to 50 atm in the temperature range 573 to 1173 K. On the basis of the equilibrium calculations the optimal conditions for generating hydrogen by SRB were reported in the temperature range from 873 to 1073 K, with S/BtOH of 9 to 12 at 1 atm. The hydrogen yield was in the range of 75.13 to 81.27% (EQ-11) with molar composition of 46.20% to 54.96% (wet basis) calculated by EQ-13. Further the effects of coke hydrogenation to methane were evaluated. Simulations were performed in two sets, i.e., primary products ("H_2, CO, CO_2 and C") including or excluding methane. These simulations were performed at 573 K and S/BtOH of 3. Results indicated that higher pressure favoured coke hydrogenation reactions at this condition i.e. 573 K and S/BtOH of 3. Coke hydrogenation to methane increased with increasing pressure up to 3 atm and decreased upon further increase in pressure. As expected, higher pressure had a negative effect on hydrogen and carbon monoxide yields. The H_2 yield (wt% fuel) calculated by the Gibbs free energy minimization method from SRB at molar steam to carbon ratio of 3 and atmospheric pressure is also plotted in Figure 2b for comparison with the other fuels reviewed (this work). Due to its lower O/C than ethanol and glycerol, its yield profile is the highest of the three.

Wang and Cao [64] reported thermodynamics of hydrogen production by sorption enhanced SRB. They performed the simulation with calcium oxide/butanol molar ratio ('CaO/BtOH') and S/BtOH in the range of 0–15, with temperatures 500–1500 K and pressures from 1–100 atm. Similarly to Nahar and Madhani [63], increases in pressure was reported to have negative effect on the process. An increase in pressure was reported to increase methanation of carbon monoxide. Highest molar concentration of hydrogen in reformates gas i.e. 97.07% (EQ-13) with 0.05% CO_2 was reported at 800 K, S/BtOH of 10 and the CaO/BtOH of 8. In comparison to SRB, sorption enhanced SRB was reported to produce less carbon monoxide i.e. 0.04 mol%. In contrast to Wang and Cao [64], Lima da silva et al. [65] reported same hydrogen molar composition i.e. 97 % (EQ-13) at higher pressure of 5 atm in sorption enhanced SRB. The authors reported the optimal conditions for hydrogen production by sorption enhanced SRB at 773 K with S/BtOH of 12 with CaO/BtOH of 4. But the thermal efficiency was lower than that reported by Wang and Cao [64]. Thermal efficiencies of 76.6 and 81.15 % were reported by the authors and Wang and Cao respectively. These thermodynamic analyses provide a starting point for the experimental investigations of SRB and sorption enhanced SRB.

Table 3 represents the performance of various investigations in terms of hydrogen yield, selectivity and molar composition for SRB.

Table 3: Investigations in terms of hydrogen yield, selectivity and molar composition for SRB.

4.2 Catalytic investigations:

At the time of this review, hydrogen production by SRB is novel and very limited numbers of catalytic investigations have been performed. SR of butanol and acetol as model compounds of bio-oil was examined at 1023 K using a nickel (Ni-Al) based co-precipitated catalyst. The performance of the process was measured in terms of wt% gases and liquids produced per butanol or acetol. 50% and 86% of carbon was converted to gases for butanol and acetol respectively [66]. The ratio of catalyst to feed flow rate (W/m_{org}) significantly influenced SR of both acetol and butanol. When W/m_{org} was increased, carbon conversion to gas, hydrogen and carbon dioxide yields increased while CH_4 and C_2H_6 diminished. The analysis of SR of 2-butanol, a component of industrial wastes from the semiconductor industry has been reported by Palmeri et al. [67]. While extremely reactive with a freshly activated catalyst, 2-butanol showed the lowest conversion of all solvents after a few hours. The greater stability of the carbonylic functional groups as compared to hydroxylic entities and the direct relationship between poisoning due to coke formation and the carbon atom number of the substrate explained the rapid deactivation with 2-butanol. Due to the limited catalytic investigations, more evaluations of SRB need to be performed to get a real picture of the process.

5. Steam reforming of bio-oil and its model compounds:

Hydrogen can be directly produced from biomass by the process of gasification [68, 69]. However the use of biomass by this process suffers disadvantages like storage, transportation and energy density. An alternative approach to use biomass by its conversion into a bio-oil (in contrast with “fossil oil”), by fast pyrolysis have been devised [70-72]. Bio-oil is a complex mixture containing aldehydes, ketones, carboxylic acid, phenols and lignin fragments depending on the source of biomass. A typical composition of bio-oil from wood is water (20–30%), lignin fragments (15–30%), aldehydes (10–20%), carboxylic acids, carbohydrates (5–10%), phenols (2–5%) [73]. Any source of biomass can in principle be used for the production of bio-oils, with many examples in the literature, e.g. elephant grass, rice husk, palm empty fruit bunches, eucalyptus [74-77]. Since conversion of bio-oil to usable fuel requires further processing [78], several studies involving direct SR of bio-oils to convert synthesis gas produced to transportation fuels have been performed [79-83]. As the experiments on SR experiments of bio-oil obtained from pine and palm oil fruit bunches was investigated these bio-oil were mainly considered for the catalytic evaluations in preceding sections.

Table 4 represents the performance of various investigations in terms of hydrogen yield, selectivity and molar composition in the SR of bio-oil.

Table 4: Investigations in terms of hydrogen yield, selectivity and molar composition in the SR of bio-oil.

5.1 Thermodynamic investigations:

Vagia and Lemonidou[84] examined the thermodynamics of the steam reforming of acetic acid (SRA), ethylene glycol (SREG) and acetone (SRAC) as model compounds for bio-oils. Notwithstanding thermodynamic limitations, the maximum theoretical yields by combined SRA, SREG and SRAC with WGS are 13.3 wt% at molar steam to fuel ratio S/A of 2, 16.1 wt% at S/EG of 2, and 27.6 wt% at S/AC of 5 respectively. The analysis was carried out by Gibbs free energy minimization method by varying the temperature (400–1300 K), steam to fuel ratio (1–9) and pressure (1–20 atm). They reported the highest hydrogen yield in SRA in comparison to SREG and SRAC, with S/A, S/EG and S/AC of 6, 6 and 9 respectively at 900 K. Hydrogen yields of 84.76, 79.46 and 84.44% (EQ-14-16) were reported in SRA, SREG and SRAC respectively. On a fuel mass basis, with 23.3 wt%, the yield of SRAC would therefore have been higher than the other fuels, and with 11.3 wt%, SRA would have the lowest. Methane selectivity was reported to be highest in SRAC and lowest in SRA respectively. In contrast to Vagia and Lemonidou, Aktaş et al.[85] reported a higher hydrogen mole fraction even at pressure as high as 30 atm in SR of model bio-oil components like isopropyl alcohol, lactic acid and phenols. These results are in contradiction to most of the authors in SR of various liquid fuels like ethanol, glycerol and butanol [16, 43, 63]. The authors reported the best operating conditions a steam-to-fuel ratio of 4, 5 and 9 at

1200 K for isopropyl alcohol, lactic acid and phenols respectively. Figure 2b features the H_2 yield of acetic acid (in the conditions described earlier), with, below that of glycerol, the lowest of the yields from the fuels reviewed.

5.2 Catalytic investigations:

Hu and Lu [79] investigated the SRA for hydrogen production over 20 wt% transition metals (Ni, Co, Fe or Cu) supported on Al_2O_3 catalyst. Ni/Al_2O_3 and Co/Al_2O_3 were reported to have high activity in comparison with Fe/Al_2O_3 and Cu/Al_2O_3. The difference in catalytic activity was attributed to the cracking activity of the metals toward the C–C and C–H bonds of acetic acid. The experiments were carried out in the temperature range of 573–873 K with S/A of 15, liquid hourly space velocity (LHSV) of 8.3 h^{-1} and 1 atm. The Ni/Al_2O_3 exhibited a more stable activity than the Co/Al_2O_3 catalyst. Significant coke deposition and oxidation of metallic phase was observed over the Co/Al_2O_3, leading to catalyst deactivation. Coke formation over nickel based catalyst involves an adsorbed acetate species that decarboxylates to form the coke precursor, ($CH_{1–3}$) and also ketene, a dehydration product of acetic acid that decomposes to form ($CH_{1,2}$) [72].

On the contrary to Co/Al_2O_3, much slower coke formation and metal sintering rates with much higher resistivity of active metal toward oxidation was attributed to the stability of the Ni/Al_2O_3 catalyst. The Co/Al_2O_3 catalyst was more active for the reverse water gas shift reaction and the decomposition of acetic acid to CO. In contrast, the Ni/Al_2O_3 catalyst was more active for methanation reactions and the decomposition of acetic acid to methane, leading to higher methane formation at mild temperatures. The Ni/Al_2O_3 was also active in SR of methane and performed well under harsh S/A. Over nickel based catalyst.

Basagiannis and Verykios [82] evaluated SRA as a model component of pyrolysis oil. The influence of several parameters which included catalyst composition, i.e. nature of the metal and the carrier, reaction temperature and time-on-stream on the catalytic activity and the selectivity were examined. Noble metals such as Pt, Pd, Rh, Ru and Ni supported on metal oxides like Al_2O_3, La_2O_3/Al_2O_3, MgO/Al_2O_3 and CeO_2/Al_2O_3 prepared by the impregnation method were investigated. A metal loading from 0.5 to 17 wt% over the temperature range of 823-1123 K with S/A of 3 was used for the investigations. Among the catalysts investigated, the Ni based catalysts exhibited the highest activity as a result of high metal loading. The order of activity 17 wt% Ni/Al_2O_3>0.5wt% Rh/Al_2O_3>1wt% Ru/Al_2O_3>1wt% Pd/Al_2O_3>1wt% Pt/Al_2O_3 was reported. Similarly, the Ni based catalyst exhibited highest hydrogen selectivity even below 873 K; with zero hydrogen selectivity over Ru, Pt and Pd below 873 K. The Rh based catalyst promoted ketonization and the reverse WGS reaction. Pt based catalyst promoted water gas shift in comparison to Rh based catalyst. Since conversion of bio-oil to usable fuel requires further processing [78]. Several studies involving direct SR of bio-oils to convert synthesis gas produced to transportation fuels have been performed [79-83].

Among the basic oxides, 15 wt % MgO promoted Al_2O_3 exhibited the best performance. Doping of Al_2O_3 seemed to promote ketonization reactions over the Ni based catalyst. In the case of Ru supported catalyst, doping the support with oxides proved to be significant in terms of catalytic activity and hydrogen selectivity in comparison to undoped catalyst. Ru based catalysts were highly stable in comparison to Ni based ones. Ru catalysts supported on La_2O_3/Al_2O_3 and MgO/Al_2O_3 carriers showed good long-term stability for about 50 h.

Dong et al.[81] investigated the formation of carbon over $Ni/\gamma\text{-}Al_2O_3$ catalyst in SRA at 873 K with S/A of 4 and WHSV of 5.01 g-acetic acid/g-cat.h. The Ni loading was varied between 3 and 15 wt%. They reported that increasing Ni loading suppressed ketonization reaction or it promoted the cracking of acetone a product obtained via ketonization reaction**.** Carbide-like carbon and graphitic-like carbon was formed on the catalysts and was affected by Ni loading. When Ni loading was increased from 9 to 15 wt%, the amount of carbide-like carbon decreased and graphitic-like carbon increased. The catalyst with 12 wt% Ni loading was reported to show higher catalytic activity and lower coke deposited rate. Similarly Lee-Langton et al.[86] performed chemical looping reforming on pine and palm empty fruit bunches derived (EFB) bio oil using an 18 wt% NiO/Al_2O_3 catalyst. Highest hydrogen yields efficiencies of 67 and 83 % (EQ-18) at 873 K with steam to carbon ratios of 2.3 and 2.7 for pine and EFB bio oils respectively (on a moisture free basis) were found for the first cycle of the tests. Hydrogen selectivity of 91 and 84 % was recorded for pine and EFB bio-oils respectively.

Rioche et al. [87] reported that the nature of the support appeared to play a significant role in the activity of the catalyst in SRA. The use of ceria–zirconia, a redox mixed oxide, exhibited higher yields as compared to Al_2O_3 supported catalysts, Rh and Pt catalyst showed high activity in comparison to Pd. The activity of the catalyst was tested at S/A of 4, in the temperature range 923-1223 K. The order of activity was reported to be 1% $Rh\text{-}CeZrO_2$ > 1% $Pt\text{-}CeZrO_2$ ~1% $Rh\text{-}Al_2O_3$ > 1% $Pd\text{-}CeZrO_2$ > 1% $Pt\text{-}Al_2O_3$ > 1% $Pd\text{-}Al_2O_3$ with comparable hydrogen yields of 66% (EQ-14). The performance of 1% $Pt\text{-}CeZrO_2$ was then evaluated for SR of bio–oil (SRBO) obtained from the fast pyrolysis of beech wood. The catalyst showed similar yields of hydrogen and CO_x as the model compounds over catalysts. A hydrogen yield above 50% was sustained for 9 h at 1103 ± 303 K with a steam to carbon ratio of 5.0 and GHSV= 3090 h^{-1}.

Yan et al. [88] examined the catalytic performance $Ni/CeO_2\text{–}ZrO_2$ for SR of aqueous fraction of bio-oil (SRABO) in the temperature range of 723-1023 K with steam/bio–oil aqueous fraction molar ratio of 4.9. Ni loading was varied between 5 and 12 wt % and the Ce between 5 and 10 wt%. A 12 wt % Ni loading with 10 wt% Ce content exhibited the best hydrogen yield, reaching the highest of 67.8% (EQ-14) and hydrogen molar content was 61.8% at 1073 K. The effect of Ce content on the performance of the process was also evaluated. Increasing the Ce content had no effect on the hydrogen molar concentration. Hydrogen yield increased with rising Ce loading from 5 to 7.5 wt %, but with further increases the yield diminished. Highest hydrogen yield of 69.7 % (EQ-14) with 61.9 mol% concentration was reported over 12 wt% Ni/ 7.5 wt% $CeO_2\text{–}ZrO_2$ catalyst, at 1023 K. The

Ni/CeO_2–ZrO_2 based catalyst hydrogen yield leveled at 35% in comparison with commercial catalyst, in stability test of 100 min.

Additions of noble metals like Rh to CeO_2-ZrO_2 have shown to increase the activity of the catalyst and decrease the formation of coke. Vagia and Lemonidou[83] studied SRA over 5 wt% Ni and 0.5 wt % Rh supported on CeO_2-ZrO_2 catalyst at 823-923-1023 K with S/A of 6. Figure 5 represents the effect of temperature on acetic acid conversion and yield of products in SRA at S/A of 6[83]. Formation of coke over bare supports was higher in comparison to supported metal catalyst. Over the Rh catalyst, the deposition rate was 0.007 mol $C_{(s)}$/mol C of acetic acid at 923 K. In comparison to the Rh based catalyst, higher coke formation was detected over the Ni based catalyst, with 0.029 $C_{(s)}$/mol C of acetic acid detected at 923 K after 3 h of SRA experiment. Carbon deposits on Rh based catalyst were strongly adsorbed carbonaceous compounds precursors of coke, which were located on the uncovered support surface. In contrast, the slightly higher coke deposits over the Ni catalyst were mostly of filamentous type probably present on the metal crystallites. Higher oxygen rates over the Ni catalyst were reported. The significantly lower activation energy of the Ni supported catalyst resulted from the higher extent of support reduction accompanied by increased number of oxygen vacancies which facilitated the oxygen mobility affecting coke deposits. A 20% loss in activity after 15 h operation was reported over $0.5Rh/CeO_2$–ZrO_2 due to sintering of Rh particles.

Like SRE and SRG, hydrogen production by SRA as a model compound of bio-oil over Ni and Rh supported on Al_2O_3 and CeO_2-ZrO_2 showed higher activity, but Ru supported on doped Al_2O_3 claimed higher stability. SRBO over CeO_2-ZrO_2 supported catalysts showed higher activity as compared to Al_2O_3. Bio-oil as a whole is a complex mixture as compared to acetic acid, having lower carbon content as compared to the real bio oil. Hydrogen production by SRBO is complex as compared to SRA; hence the stability of the catalyst would greatly depend on its ability to resist coke formation and exposure to metals in the bio-oils.

6. Steam reforming of vegetable oil:

Hydrogen production via SR of vegetable oil has been undertaken as a result of lower oxygen content, ease of transportation, low sulphur and aromatic content, higher heating value and most importantly higher hydrogen yields [89]. Vegetable oils reduce the NO_x and SO_x atmospheric levels due to its intake during the cultivation, making it beneficial in that respect [90]. In the preceding sections for complex hydrocarbons like vegetable oil or biodiesel the reactant ratios are mentioned in terms of Steam/Carbon ratio rather than reactant ratio i.e. steam/vegetable oil.

Table 5 represents the performance of various investigations in terms of hydrogen yield, selectivity and molar composition in the SR of vegetable, waste cooking oil and biodiesel.

Table 5: Investigations in terms of hydrogen yield, selectivity and molar composition in the SR of vegetable, waste cooking oil and biodiesel.

6.1 Thermodynamic investigations:

Yenumala and Maity [91] studied the SR of vegetable oil in the temperature range of 800-1300 K with varying S/C molar ratio from 1 to 10. The effects of triglyceride compositions were varied to examine the effect on hydrogen yield, three different mole fractions of tripalmitin, tristearin, and trioleate, 0.15/0.15/0.7, 0.3/0.25/0.45, and 0.7/0.2/0.1 with average molecular compositions of the mixtures $C_{56.1}H_{104}O_6$, $C_{55.2}H_{103.7}O_6$, and $C_{52.8}H_{101}O_6$ respectively. The variation of hydrogen yield with triglyceride composition was reported due to the change in hydrogen content of the triglyceride mixtures, and it decreased in the order $C_{56.1}H_{104}O_6 > C_{55.2}H_{103.7}O_6 > C_{52.8}H_{101}O_6$. Therefore, the increase in trilinolein composition of vegetable oils relative to tristearin and trioleate decreased hydrogen yield, while trilinolein relative to tripalmitin increased the hydrogen yield. The optimum operating conditions for SR of vegetable oils was reported to be 875–925 K and steam to carbon molar ratio of 5–6. Hydrogen yield of ~93% (EQ- 19) with ~12 % carbon monoxide selectivity was observed at 875 K with S/C of 5 was reported. Pimenidou et al. [92] reported the thermodynamic equilibrium of chemical looping reforming at 833- 844 K, with S/C =4/1. 100 and 37 % conversions for waste cooking oil and steam were reported respectively. Hydrogen selectivity of 70% with 5.6 and 68.7% selectivity to methane and carbon dioxide were reported. In Figure 2b, due to its lowest O/C ratio, the H_2 yield from the steam reforming of rapeseed oil appears the highest of all the fuels reviewed (this work). The rapeseed oil's composition was 65.3% oleic acid, 18.6% linoleic acid, 9.6% alpha-linoleic acid, 4.7% palmitic acid and 1.8% stearic acid (mass basis).

6.2 Catalytic investigations:

Hydrogen productions by SR from waste cooking oil using commercial 18% Ni/Al_2O_3 supplied by Johnson Matthey **[92, 93]**, virgin vegetable oil like sunflower oil also using 15 % Ni/Al_2O_3 commercial catalyst supplied by United Catalyst **[94, 95]**, rapeseed oil using same 15 % Ni/Al_2O_3 catalyst **[96]** and palm fatty acid distillates (PFAD) **[97]** using 5%$Ni/Ce\text{-}ZrO_2$ have been reported. Pimenidou et al. **[92]** studied chemical looping SR of waste cooking oil using a packed bed reactor. Chemical looping SR is processes where oxygen transfer material (OTM) as catalyst. This type of SR uses both steam and oxygen to react with fuel. The method uses fuel to reduce the oxide catalyst to pure metal followed by SR over this reduced catalyst. The SR step oxidise the catalyst to convert it to its oxide form. To close the loop, the oxygen depleted solid material must be re-oxidized before to start of a new cycle. The process of oxidation and reduction is continued till activity drops significantly. The catalyst needs regeneration which is brought about by oxidising it with oxygen or air. The S/C molar ratio of 4 and temperature in the range of 873 to 973 K yielded the best results. Six cycles at two weight hourly space velocity (WHSV) of 2.64 and 5.28 h^{-1} yielded high (>0.74) and low (<0.2) oil conversion respectively operating for 6 cycles. A WHSV of 2.64 exhibited conversions close to thermodynamic evaluations. The results indicated that under lean steam to carbon ratio i.e. 1.73, the experimental results were very poor and were very far off from the equilibrium results. But under rich steam to carbon ratios, i.e. 2.5-4, the results were close to equilibrium.

Pimenidou et al.[93] performed sorption enhanced chemical looping SR of waste cooking oil (rapeseed oil before cooking) coupled with chemical looping SR, at S/C of 4, 873 K and 1 atm. Higher fuel and steam conversion were reported in the presence of the sorbent dolomite than without it. Initially, the dolomite carbonation was very high (100%), and 98% hydrogen purity was obtained, but the extent of the carbonation decreased to around 56% with a hydrogen purity of 95% respectively in the following cycles. Reduction of the Ni catalyst occurred concurrently with SR, WGS and carbonation of the sorbent, with hydrogen produced continuously under fuel/steam feeds. Catalyst and CO_2-sorbent regeneration was reported, and a long period of operation without external heating to the reactor within each cycle was demonstrated. Figure 6 (a) shows the hydrogen purity (vol %) with time on stream during cycles 1 and 6 of sorption enhanced chemical looping steam reforming of waste vegetable oil in packed bed reactor. The electrical power input to the reactor during cycle 1 is shown below it, indicating little or no power consumption in the reactor while sorption enhancement was taking place.

Marquevich et al. [96] carried SR of four different types of oils i.e. rapeseed oil, soybean, corn oil and sunflower oil using a commercial catalyst and a hydrotalcite (HT) precursor based catalyst. The experiments were performed in an isothermal fixed-bed tubular reactor at S/C molar ratio of 3, 6 and 9 with temperatures between 773 and 873 K and high space velocities of 0.76-1.90 mol carbon/ (gcat h). Hydrogen production ranged between 0.3 to 7.5 moles hydrogen / (g_{Ni} h) depending on the operating conditions. The HT catalyst seemed promising for SR vegetable oils because of its very high activity per gram of catalyst. The performance of the catalyst at same temperature and steam/vegetable oil ratio was independent on type of vegetable oil. Similarly authors prepared a hydrotalcite like precursor catalyst, with an Ni/Al atomic ratio of 2/1, that was suitable for SR of sunflower oil at the same operating conditions and compared it with two commercial catalysts for SR hydrocarbons (ICI 46/1 and UCI G90C). The HT catalyst had almost 10 times more catalytic activity than the commercial catalysts [94]. A reaction mechanism was reported. Organic molecules (fatty acids) were adsorbed on the metal sites, while the steam molecules were preferentially adsorbed on Al_2O_3. The optimum situation was when steam was adsorbed on the support and reacted in the metal interface with the organic that adsorbed there, but as the partial pressure of steam increased H_2O molecules competed with organic molecules for sites [94].

Shotipruk et al. [97] showed that Ni/Ce–ZrO_2 catalyst prepared by cationic surfactant-assisted method (Ce–ZrO_2 (‘high surface area’)) with Ce/Zr = 3/1 provided the highest degree of oxygen storage capacity (OSC) and SR reactivity with greatest resistance toward carbon deposition in SR of palm fatty acids distillate (PFAD) at 1173 K. The main products from the SR of PFAD over Ce–ZrO_2 (high surface area-'HSA') were H_2, CO,CO_2 and with some amounts of CH_4, C_2H_4, and C_2H_6. Higher hydrocarbons were eliminated by increasing temperature up to 1273 K. The addition of either oxygen or hydrogen together with PFAD and steam considerably reduced the degree of carbon deposition. The presence of O_2 also reduced the formations of hydrocarbons, on the other hand, these formations increased when hydrogen was introduced at the feed. The negative effect of hydrogen was due to hydration reaction as well as the reduction of lattice O_2 by hydrogen which consequently inhibited the reaction of lattice O_2 with surface hydrocarbon species.

Formation of carbon is a complex phenomenon in case of vegetable oil and various reactions are responsible for the formation of coke resulting in catalyst deactivation. Cracking of oils is a important phenomenon which affects the formation of coke and catalyst activity. When oil is heated above 573 K, fatty acids are liberated by cleavage of the ester bonds [96]. At higher temperatures fatty acids fatty acids decompose via decarboxylation and decarbonylation to saturated and unsaturated hydrocarbons, liberating carbon oxides. These hydrocarbons are then further converted by ethylene elimination, isomerization, and hydrogen-transfer reactions to yield ethylene, propylene, and other small hydrocarbons, which are coke precursors. Along with this mechanisms there are some other reactions involved which are taking place and resulting in the formation of coke [98, 99]. In depth analysis of these mechanisms is examined by Adjaye and Bakhshi [100], Adebanjo et al.[101], Katikaneni et al. [102-104].

Most of the studies of the studies of SR of vegetable oil have shown to have potential for hydrogen production. But the availability and prices of the oil would be a concern for the commercial viability of the process. Further, the use of virgin oils like sunflower or rapeseed raises the question of food vs. biofuel. Use of non-edible oils like waste cooking oil, jatropha curcas and karanja can be utilized as a non-food feedstock.

7. Steam reforming of biodiesel:

Raw or refined vegetable oil can be directly utilized in a modified engine but it has serious drawbacks. Raw or refined vegetable oil, or recycled greases have significantly different and widely varying properties that are not acceptable for use in modern diesel engines. Vegetable oil has higher viscosity and chemical composition of unprocessed oils and fats have been shown to cause problems in a number of areas including piston ring sticking, deposits on the injector and combustion chamber, fuel system deposits, resulting in reduced power, reduced fuel economy and increased exhaust emissions [105]. In comparison, biodiesel has the advantages of lower viscosity, no engine modification requirements, low sulphur (<0.001%), natural lubricant properties compared to petrodiesel resulting in less engine wear. Biodiesel consists of mono-alkyl esters of long-chain fatty acids derived from the triglycerides (TG) making up vegetable oils or animal fats which can be substituted for diesel fuel. Biodiesel is prepared by reacting vegetable oil or animal fats with methanol in presence of acid (esterification) or an alkali (transesterification) resulting in the formation of methyl esters of fatty acids and glycerol [106-108]. Acid catalyst systems are characterized by slow reaction rates and high alcohol: TG requirements (20:1 and more). Generally, acid catalyzed reactions are used to convert free fatty acids (FFA) to esters, or soaps to esters as a pretreatment step for high FFA feedstocks. The pretreated oil can be transesterfied in presence of alkali and excesses methanol (6:1) resulting the formation of esters[109]. The composition of biodiesel varies with type of vegetable oil or animal fats used. Oils like rapeseed (canola) and olive oil have oleic acid as the major component in comparison safflower; soybean, sunflower and walnut have linoleic acid as the major component. Among the virgin oils coconut oil has different composition with Lauric acid being the major one. The typical composition of the common used oil and animal fats is given in [110, 111].

7.1 Thermodynamic investigations:

At the time of this review, only thermodynamic analyses of the hydrogen production by SR of biodiesel had been performed. Sgori et al., Specchia et al., and Kraaij et al. [5, 112, 113] proposed various processes for developing a fuel processor for biodiesel fuelled fuel cells. Simulations were carried out and autothermal reforming (ATR) was selected as the best option. Similarly Martin and Wolmer [1] also showed that the ATR concept with heat integration is competitive with the SR concept with heat integration in terms of fuel processing efficiency and overall system efficiency. In ATR reaction mode the heating is done directly by using partial oxidation reactions. Hence the hydrogen yield and selectivity would be lowered as compared to SR.

Nahar [111] examined the thermodynamics of SR and ATR of biodiesel (i.e. soybean oil methyl ester (SOME)) for hydrogen production, evaluated using the Gibbs free energy minimization method with S/C molar ratio of 0.16 to 0.64, O_2/C molar ratio from 0 to 0.25 and reaction temperature from 573-873 K. From the results S/C $\geq$0.48 and O_2/C of 0.25 were the best conditions to operate the ATR reformer at solid oxide fuel cell (SOFC) temperature i.e. 1073 K. Hydrogen yields of 76.97 and 74.38 % (EQ-23) were reported with S/C of 0.64 for SR and S/C of 0.64 along with O_2/C of 0.25 at 1073 K for ATR respectively. The carbon monoxide yield was lower under SR conditions as compared to ATR conditions. This could be due to the oxidation of coke to carbon monoxide as result of introduction of oxygen. Carbon monoxide yields of 91.66 and 63.74 % were reported at steam/SOME=9/1, oxygen/SOME of 4.8 for ATR and steam/SOME of 12 for SR respectively. Further the simulations revealed that transesterification contributed to increase in hydrogen and methane formation. Alkane selectivity decreased with increase in carbon number of the esters while coke formation increased with carbon number. Alkene and alkane selectivity were found to be lower under ATR as compared to SR conditions. A coke free environment was obtained under ATR conditions in comparison with SR, under the conditions investigated. Figure 2b shows the H_2 yield from steam reforming of a blend of fatty acid methyl esters obtained from the esterification of the rapeseed oil previously modeled (for each fatty acid in the rapeseed oil, the same mol fraction of the corresponding fatty acid methyl ester was used for the initial mixture). The yield curve with temperature obtained for the FAME mixture was so close to that of its fatty acids source mixture as to be indistinguishable and featured the highest yield of all fuels reviewed.

8. Catalytic evaluations:

At the time of this review, only one study reporting SR of biodiesel s available. It was carried out by Abatzoglou et al.[114] who investigated the SR of biodiesel derived from vegetable oil over 5%-$NiAl_2O_4/Al_2O_3$ (50%)-(50%) YSZ (yttria-stabilized zirconia). The authors did not specify the type of oil used in the preparation of the biodiesel. A biodiesel water emulsion was prepared with S/C varying from 1.9 to 2.4 in the temperature range of 973-998 K with GHSV varying between 8,700- 13500 cm^3/g h. The authors reported that conversion increased with increase in temperature, with 100 % conversion achieved at 998 K. At this temperature conversion decreased with increase in S/C ratio as a result of increase in GHSV. Hydrogen molar composition of ~70 % was reported. Deactivation of the catalyst due to sintering was reported rather than by coking.

9. Acknowledgement:

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10. Executive Summary:

SR is the one of the most promising processes for liquid fuel conversion to hydrogen from feedstock of biomass origin as a result of its high efficiency. Renewable liquid fuels can be directly converted to a hydrogen rich gas mixture and further processed based on the type of fuel cells to be utilized. Relatively short chain oxygenated and single compound hydrocarbons from the examined liquid fuels like ethanol and butanol can be suited for generating hydrogen for PEMFC. Complex hydrocarbon mixtures like crude glycerol, bio-oil, biodiesel and vegetable oil would be suitable for SOFCs. Since these fuels could produce significant amounts of CO and even CH_4, which SOFCs, could be effectively utilized as fuel.

10.1 Hydrogen production via SRE:

Thermodynamic evaluations of steam reforming of ethanol (SRE) have shown that the best conditions steam to ethanol molar ratios from 3-6 at 900–1200 K with hydrogen yield of 60.52-83.58% and molar composition of 61.48–71.49% at atmospheric pressure.

10.2 Hydrogen production via SRG:

The best conditions by thermodynamic analysis for hydrogen production via steam reforming of glycerol (SRG) were reported to in the temperature range of 600-1000 K, with hydrogen yield of 88.71 % and molar composition of 60% at S/G ratio of 9 and atmospheric pressure.

10.3 Hydrogen production via SRB:

On the basis of the equilibrium calculations the optimal conditions for generating hydrogen by steam reforming of butanol (SRB) were reported in the temperature range from 873 to 1073 K, with S/BtOH molar ratios between 9 to 12 giving a hydrogen yield of 75.13-81.27 % and molar composition of 46.20-54.96 at 1023 K at atmospheric pressure.

10.4 Hydrogen production via SR of bio-oils:

Since bio-oil is a complex mixture the optimal conditions are based on model components. Based on the thermodynamics of the steam reforming of acetic acid (SRA), ethylene glycol (SREG) and acetone (SRAC), the optimal conditions for hydrogen production were reported to be at 900 K, with S/A of 6, S/EG of 6 and S/AC ratio of 9 respectively at atmospheric pressure. Hydrogen yields of 84.76, 79.46, and 84.44% were observed at these conditions for acetic acid, ethylene glycol, and acetone respectively.

10.5 Hydrogen production via SR of vegetable oil and biodiesel:

Hydrogen production from vegetable oil is investigated by quite a few researchers in comparison to biodiesel. The optimum operating conditions for SR of vegetable oils was reported to be 875–925 K S/C of 5–6 with hydrogen yield of ~95%. Hydrogen yields of 76.97 and 74.38 % (EQ-23) were reported with S/C of 0.64 for SR and S/C of 0.64 along with O_2/C of 0.25 at 1073 K for ATR respectively.

Noble metals like Rh have exhibited good performance in SR of the most of the alcohols like ethanol, glycerol, and bio-oils. Although noble metals have activity as SR catalyst but due to economic reasons these catalyst are not preferred. In comparison Ni based catalysts show good promise and these are commercially used. Cerium based catalyst supports have shown encouraging results in SR of most of the alcohols and complex hydrocarbons like bio-oils and vegetable oils. These supports have various advantages over others like Al_2O_3. Cerium based supports have shown to have good stability, high conversion and lower side reactions. For e.g. formation of C_2H_4 by dehydration of ethanol leading to catalyst deactivation in SRE. These mixed oxide based catalysts have shown high conversion at low temperatures i.e. 873 K. Further the redox stability and oxygen storage capacity of the catalyst support help in minimizing the coke deposition leading to longer life. In addition to higher reducibility of NiO, higher dispersion and metal loading over ceria based catalyst would promote better catalytic activity. Since there are no catalytic evaluations of hydrogen production via SR of biodiesel and butanol Ni based catalyst over cerium based supports can be promising catalyst for hydrogen production.

11. Future perspective:

All the feedstocks examined offer a range of advantages. Ethanol offers medium hydrogen yield but in countries which already use transport fuel (Brazil, USA), using ethanol as a hydrogen source would benefit from an infrastructure already in place. Glycerol may offer one of the lowest hydrogen yields but with crude glycerol increasingly becoming a waste issue, conversion to hydrogen is a valid proposition. Butanol and biodiesel present the highest hydrogen yields, and despite their origin from energy crops which currently create land competition with food crops, may in the future switch to use aquatic biomass as their primary source. Both butanol and biodiesel are amongst the least liquid feedstock explored for hydrogen production. Companies like BP an Dupont have already started marketing it in the UK [63, 115] and companies like Gevo Inc, have retrofitted an ethanol producing plant to produce butanol [116]. Considerable efforts have been put in development of waste cellulosic materials as feedstocks for production of butanol as compared to avoid completion with food sources like grain barley or sugar cane. Developments in genetic engineering for strain development, and butanol recovery processes for the production of butanol have been widely explored [61, 117].

Biodiesel produced from microalgae is an unlimited resource and has the potential for yields 50–100 times greater than biodiesel from soybeans [118]. Microalgae can utilize waste CO_2 from fossil-fueled power plants and other high carbon emitting facilities. These efforts show us that availability of biofuels like butanol and biodiesel will increase ensuring supply in future. The use of fresh vegetable oil for production of hydrogen would be midcult as a result of direct competition with food. However vegetable oil for the frying of food is limited to one or few uses, after which the waste oil is fit to be used as an energy carrier, either as biodiesel feedstock, which generates crude glycerol waste, or for hydrogen production. The future of crude glycerol as feed stock is uncertain since most it comes from transesterification of fats and oils. New processes for production of glycerol-free biodiesel have been investigated and emerging to replace the existing process [119-121]. Bio-oil usage and future availability are currently unknown. The advantage of bio-oils is the diversity of feedstock from which they can be derived, including agricultural and industrial wastes and the simplicity of the fast pyrolysis process that creates them, alleviating dependency on foreign imports of fossil fuels.

Recently micro reactor technology is becoming very popular and several successful investigations of hydrogen production in micro reformers have been conducted [122]. In microreactors high heat and mass transfer rates are established due to the high surface-to-volume ratios and short transfer distances in the reactors. For reactions that operate in mass and heat transfer-limited regimes, microreaction smaller devices could be designed as compared to conventional counterparts at the same throughput. Due to smaller size they can be easily used for automotive or other space limited applications. Innova Tek, USA and Chevron have collaborated for the production of hydrogen from biodiesel in micro reformers [123, 124]. Micro reformers fuelled with biofuels like biodiesel or biobutanol have distinct possibility of commercialization in near future.

Although SR processes produce the highest amount of hydrogen, SR is an endothermic reaction and requires lot of heat for the reaction to proceed. In large scale production of hydrogen from feedstocks like natural gas or naphtha, which account for most of the current world hydrogen production, giant externally fired tubular reactors are used. The major disadvantage of this process is heat transfer in these tubular reactors which are made of high nickel content special stainless steel. Hot spots tend to develop with inhomogeneous heat transfer, affecting the life of the catalyst and the tubes. The material is used for the tubes i.e. creep resistant austenitic steel HK grade is expensive. The life the tubes are greatly dependent on the service conditions. Due to prolonged exposure to high temperature, the microstructure of the material is subjected to degradation. For e.g., in the early stages carbides precipitate from the steel. Following this, there is reduction in strength and embrittlement due to coalescence and coarsening of the carbides [125]. Operating 20 °C above the nominal temperature is known in industry to reduce by half the lifetime of these very expensive reformer tubes. Therefore it is necessary to develop SR technologies to address this major drawback of the processes. For small scale reforming applications like distributed power, or APUs for mobile applications, ATR has been shown to be a promising option to produce hydrogen [1, 5]. In case of stationary fuel cells, hydrogen production technologies like chemical looping SR and sorption enhanced SR are gaining importance. These processes have advantages over conventional SR in that they couple together exothermic reactions with the SR within the reformer resulting lower heat duty and eliminate the need for inefficient and inhomogeneous external heating from flame to reformer tube. They also rely heavily on process integration, reducing the number of steps required to produce hydrogen of high purity. These processes also have great fuel flexibility, allowing the switching from one to another feedstock according to availability. The major challenges for these processes would be in the achieving the same lifetimes of oxygen transfer materials and CO_2 sorbents than those of the current generation of SR catalysts.

Abbreviations and Nomenclature:

ATR- Autothermal reforming

BO- Bio oil

CHP- Combined heat and power

HSA- High surface area

LHSV- Liquid hourly space velocity

PFAD -Palm fatty acid distillates

PEMC -Polymer electrolyte membrane fuel cells

PO- Partial oxidation

SR- Steam reforming

SRAC-Steam reforming of acetone

SRA- Steam reforming of acetic acid

SRABO- Steam reforming of aqueous fraction of bio oil

SRBO- Steam reforming of bio oil

SRB-Steam reforming of butanol

SRE- Steam reforming of ethanol

SREG- Steam reforming of ethylene glycol

SRG- Steam reforming of glycerol

WHSV -weight hourly space velocity

The nomenclature used by various authors for analysis of thermodynamic and experimental results is below.

Wang and Wang [16] defined hydrogen yield in thermodynamics of SRE as below

$$Y_{H_2}(\%) = \frac{F_{H_2out}}{\left(6\times F_{ein}\right)}\times 100 \tag{5}$$

Where F_{ein} is the molar flow rate of ethanol at inlet and outlet, respectively, and F_{H2out} is the molar flow rate of hydrogen at outlet. While ($6\times F_{ein}$) is the theoretical mole ratio of ethanol feed and hydrogen produced.

The formula used by Adhikari et al.[43], Buffoni et al. [49] and Chen et al.[44] for the calculation of hydrogen yield is as below.

$$Y_{H_2}(\%) = \frac{F_{H_2out}}{\left(7\times F_{gin}\right)}\times 100 \tag{6}$$

Where F_{gin} is the molar flow rate of glycerol at inlet and outlet, respectively, and F_{H2out} is the molar flow rate of hydrogen at outlet. While ($7\times F_{gin}$) is the theoretical mole ratio of ethanol feed and hydrogen produced.

Dave and Pant [55] defined the yield of hydrogen in SRG as below

$$Y_{H_2}(\%) = \frac{\text{moles of hydrogen produced}}{\text{moles of glycerol in feed}}\times 100 \tag{7}$$

In SRG Chen et al.[44] defined hydrogen selectivity by EQ-8 while Adhikari et al.[47], al. [47], Dave and Pant [55] and Zhang et al. [50] defined by EQ-9.

$$S_{H_2} = \left(\frac{2\dot{n}_{H_2out}}{(2X_{H_2Oin}\dot{n}_{H_2O} + 8X_{glyin}\dot{n}_{glyin})}\right)\times 100 \tag{8}$$

$$S_{H_2} = \left(\frac{\text{moles of hydrogen produced}}{(\text{moles of } C \text{ in gas phase} \times \text{R})}\right) \times 100 \tag{9}$$

Where R=H_2/CO_2 ratio.

Iriondo et al. defined the molar composition of hydrogen, carbon monoxide, carbon dioxide as

$$S_{H_2} = \left(\frac{\text{moles of hydrogen produced}}{(\text{moles of Glycerol feed})}\right) \tag{10}$$

Similarly to above authors Nahar and Madhani [63] defined hydrogen and carbon monoxide yield in the SRB as below

$$Y_{H_2}(\%) = \frac{F_{H_2out}}{\left(12 \times F_{bin}\right)} \times 100 \tag{11}$$

$$Y_{CO}(\%) = \frac{F_{H_2out}}{\left(4 \times F_{bin}\right)} \times 100 \tag{12}$$

Molar composition of products in SRB and sorption enhanced SRB is defined by Bimbela et al.[66], Lima da silva et al.[65], Nahar and Madhani[63] and finally Wang and Cao [64] and is as below

$$M_p(\%) = \frac{mol_p}{\sum mol_{sp}} \times 100 \tag{13}$$

Where mol_p represents the moles of each product, and mol_{sp} represents the of sum moles of products.

The definition of hydrogen yields in SRA, SREG and SRAC used by Vagia and Lemonidou [84] was as same as the one used by other authors. Same definition was used by Roiche et al. [87] and Yan et al. [88] in SRBO model components.

$$Y_{H_2}(\%) = \frac{F_{H_2out}}{\left(4 \times F_{aceticin}\right)} \times 100 \tag{14}$$

$$Y_{H_2}(\%) = \frac{F_{H_2out}}{\left(5 \times F_{ethylenein}\right)} \times 100 \tag{15}$$

$$Y_{H_2}(\%) = \frac{F_{H_{2out}}}{\left(8\times F_{acetonein}\right)}\times 100 \tag{16}$$

Dong et al.[81] and Hu and Lu [79] defined hydrogen yield and selectivity in SRA as follows

$$Y_{H_2} or S_{H_2} = \left(\frac{\text{moles of hydrogen produced}}{\text{(moles of acetic acid feed)}\times 4}\right)\times 100 \tag{17}$$

Lee-Langton [86] defined yield of hydrogen in SR of pine and empty palm oil fruit bunches derived bio oil as

$$Y_{H_2} = \left(\frac{\text{moles of hydrogen produced}}{\text{(moles of carbon in feed)}}\right) \tag{18}$$

Yenumala and Maity [91] defined hydrogen yield in SR of vegetable oil as below

$$Y_{H_2} = \left(\frac{\text{moles of hydrogen produced}}{\text{156.25(moles of vegetable oil reacted)}}\right)\times 100 \tag{19}$$

Pimenidou et al. [93] defined waste cooking oil conversion and hydrogen purity by EQ-20 and 21.

$$n_{H_2} pur = \frac{measured Y_{H_2}}{(equailbrium Y_{H_2})}\times 100 \tag{20}$$

$$X_{wo}(\%) = \frac{mol_{CO} + mol_{CO_2} + mol_{CH_4}}{(n\times \dot{n}_{woin})}\times 100 \tag{21}$$

In most of the investigations the conversion of ethanol, glycerol, butanol, and bio-oil model components was defined as below

$$X_{et}(\%)\frac{ethanol_{in}-ethanol_{out}}{ethanol_{in}}\times 100 \tag{22}$$

In thermodynamics of SR and ATR of biodiesel the definitions used for hydrogen and carbon monoxide was as below [111].

$$Y_i(\%)=\frac{F_i}{\left(x_i\times F_i\right)}\times 100 \tag{23}$$

Where Y_i is the yield of either hydrogen or carbon monoxide, F_i is the molar flow rate of either hydrogen or carbon monoxide at the outlet and x_i is the stoichiometric yield, 35.1 to 35.5 for H_2 and 13.97 to 18.91 for CO depending on the type of methyl ester.

The definition of molar composition used by various authors like Adhikari et al. [43, 47], Alberton et al.[21], Chen et al.[44], Cui et al.[45], Fajardo et al.[30], Fatsikostas et al.[22], Hu and Lu [126], Laosiripojana and Assabumrungrat [31], Marquevich et al.[94], Nahar [111], Srinivas et al.[35], Vagia and Lemonidou [84],Zhang et al.[50] in SRE, SRG and SRB also He et al. who defined purity of hydrogen using the same formula used by other authors to define molar composition as below

$$M_p(\%)=\frac{mol_p}{\sum mol_{sp}}\times 100 \tag{24}$$

Where mol_p represents the moles of each product, and mol_{sp} represents the of sum moles of products.

Hydrogen purity is defined as

$$H_2\text{purity }(\%) = \left(\frac{\frac{m}{2}+2n-k}{\frac{m}{2}+3n-k}\right)\times 100 \tag{25}$$

E.g. of hydrogen yield calculations

Hydrogen yield calculation for SRB at S/BtOH 12 at 873 K calculated by Nahar and Madhani [63] using EQ-11.

$$Y_{H_2}(\%) = \frac{9.923}{(12 \times 1)} \times 100 = 82.68\% \tag{26}$$

Similarly in case of glycerol the yield calculated by Adhikari et al.[43] using EQ-6.

$$Y_{H_2}(\%) = \frac{6}{(7 \times 1)} \times 100 = 85.71\% \tag{27}$$

KEYWORDS/ DEFINITIONS

Hydrogen, production, liquid, Biofuels, steam reforming, catalytic,

Conversion of fuel is defined by the following equation

$$X_{et}(\%) \frac{Fuel_{in} - Fuel_{out}}{Fuel_{in}} \times 100 \tag{28}$$

Conversion of fuel defines the amount of fuel converted to products and by products.

Yield of hydrogen is defined as below. Yield of hydrogen is one of the most important parameter since it explains the amount of hydrogen that can be produced from the fuel. This parameter can be used to compare the amount of hydrogen produced from various fuels by the same processes SR in this evaluation.

$$Y_{H_2}(\%) = \frac{F_{H_2 out}}{(x \times F_{fuelin})} \times 100 \tag{29}$$

Where the F_{H2} is the molar flow rate of hydrogen produced and the denominator $x \times F_{fuelin}$ is the theoretical mole ratio of fuel feed and hydrogen produced by SR.

The important factor that affects the performance of the SR processes is S/C ratio. The common definition used is

$$S/C = \frac{\dot{n_s}}{\left(\dot{n_c}\right)} \tag{30}$$

Where $\dot{n}_s$ is moles of steam and $\dot{n}_c$ is moles of carbon in the feed. For continuous systems molar flow rates can also be used in place of moles. This ratio actually defines the amount fuel and steam entering a steam reformer and it can influence the performance of the reformer in terms of amount of hydrogen being produced.

Selectivity is another important parameter used to describe the performance of SR reaction. It explains the amounts of desired product obtained and the amount of undesired products formed. In case of SR methane is obtained as a by-product. Hence selectivity for hydrogen can be defined as below.

$$S_{H_2}(\%) = \frac{F_{H_2}}{\left(F_{H_2} + F_{CH_4}\right)} \times 100 \tag{31}$$

Hydrogen molar composition or purity is another definition used by authors in this field to define the amount of hydrogen produced in comparison to other products.

$$M_{H_2}(\%) = \frac{mole_{H2}}{totalmoles} \times 100 \tag{32}$$

	Table 1										
		Conditions			Definition			Reported values			
References	Catalytic/ Thermodynamic investigation	Catalyst	S/EtOH	\ Temp (K)	Yield Y (%)	Selectivity S (%)	Molar comp M_p (%)	Y (%)	S (%)	M_p (%)	
[16]	Thermodynamic	-	3-6	900-1200	5	N/A	24	60.52-83.58	N/A	100%	61.48–71.49
.[21]	Catalytic	16%-Ni/γ-Al_2O_3	3	873	N/A	N/A	24	N/A	N/A		56
		8%-Ni/ γ-Al_2O_3									57
		16%-Ni/α-Al_2O_3								80	10
		8%-Ni/ α-Al_2O_3								>85	14
[36]	Catalytic	30%-Ni/$Ce_{0.74}Zr_{0.26}O_2$	3	873	N/A	N/A	N/A	N/A	N/A	98.7	N/A
.[22]	Catalytic	17%-Ni/γ- La_2O_3	3	1023	N/A	N/A	24	N/A	N/A		
		17%-Ni/ Al_2O_3								100	90for100h
		17%-Ni/YSZ								100	90for45 h

		17%-Ni/ MgO								100 100	90for 24 h 80for25 h
[30]	Catalytic	0.5%- Ni/CeO_2	3	598, 673 773	N/A	N/A	24	N/A	N/A	~27@598K 100@673 K -100@773K	80 for 300min 60for300min 76for300 min
[31]	Catalytic	5%- Ni/CeO_2	3	1073	N/A	N/A	24	N/A	N/A	100\	>70for100 h
[35]	Catalytic	40%-Ni/$Ce_{0.3}Zr_{0.3}O_2$	8	823	N/A	N/A	24	N/A	N/A	95	68 for 5 h

	Table 2										
		Conditions			Definition			Reported values			
References	Catalytic/ Thermodynamic investigation	Catalyst	S/G	\ Temp (K)	Yield Y (%)	Selectivity S (%)	Molar comp M_p (%)	Y (%)	S (%)	Conversion (%) -EQ 21	M_p (%)
[43]	Thermodynamic	N/A	9	600-1000	6	N/A	24	85.71	N/A	100	>35
[44]	Thermodynamic	N/A	9	923	N/A	N/A	24	88.71	86	100	>60
[45]	Thermodynamic	N/A	5	923	6	N/A	24		90.42	100	>25
[47]	Catalytic	15%-Ni/MgO 15%-Ni/CeO_2 15%-Ni/TiO_2	6	923	6	9	N/A	56.51 65.64 53.58	62.60 33.44 46.99	65.64 53.58 62.60	N/A
[44]	Catalytic	KATALCO CRG-LHR	9	673-873 ,		8	24	88.57	100@873 K	>90@873 K	~58
[55]	Catalytic	15%-Ni/CeO_2 15%-Ni/$Ce_{0.74}Zr_{0.26}$	45	973	3	9	24	3.4	59.81	94.1	

		O_2						3.9	62.53	100	
[51, 52]	Catalytic Pure glycerol Crude glycerol	18% NiO/Al_2O_3 catalyst +dolomite 18% NiO/Al_2O_3 catalyst +dolomite	9 3[1]	873-973 873-973	6	8	24	N/A N/A	68@873 K	100@873 K 100@773 K 96@773 K 96@773 K	90 97 64 88.2
[54]	Catalytic	1.3%-Ni/CeO_2 12.6%-Ni/Al_2O_3 11.9-Ni-4.3Ce%/ Al_2O_3 12.8-Ni 8.4Ce%/ Al_2O_3 12.7-Ni-17.1Ce%/ Al_2O_3	45	773-873	6	N/A	24	20 97.14 80 ~ 78 ~30	N/A	>95% for 2 h 100% for 8 h	1.4for 2 h >6.8for 8 h 6.5 >5.5 >2
[50]	Catalytic	2%-Ir/CeO_2 15%-Ni/CeO_2 15%-Co/CeO_2	9	823	6	9	24	N/A	94.1 90.8 93.4	100 100 100	68.7 67.9 68.5

1- S/C ratio

	Table 3										
		Conditions			Definition			Reported values			
References	Catalytic/ Thermodynamic investigation	Catalyst	S/BtOH	\ Temp (K)	Yield Y (%)	Selectivity S (%)	Molar comp M_p (%)	Y (%)	S (%)	Conversion (%) -EQ 21	(M_p %)
[63]	Thermodynamic	N/A	1-18	573-1173	11	N/A	13	75.13-81.27	N/A	100	46.20-54.96at 1023 K
[64]	Thermodynamic	N/A	0-15	500–1500	N/A	N/A	13	N/A	N/A	100	97.07 at 1023K
[18]	Thermodynamic	N/A	1-14	500-1450	N/A	N/A	13	N/A	N/A	100	99.06 at 848 K
.[66]	Catalytic	33%Ni-(Ni-Al)	56.4	923	N/A	N/A	13	N/A	N/A	100	73.42 for 2 h

	Table 4										
		Conditions			Definition			Reported values			
References	Catalytic/ Thermodynamic investigation	Catalyst	Steam/bio-oil	\ Temp (K)	Yield Y (%)	Selectivity S (%)	Molar comp M_p (%)	Y (%)	S (%)	Conversion (%) -EQ 21	M_p (%)
[84]	Thermodynamic Acetic acid Acetone Ethylene glycol	N/A	6 9 6	900	14 16 15	N/A	24	84.76 79.46 84.44	N/A	100 100 100	>60 >65 >65
[82]	Catalytic Acetic acid	0.5%-Rh/Al_2O_3 1%-Pt/Al_2O_3 1%-Pd/Al_2O_3 1%-Ru/Al_2O_3 17%-Ni/Al_2O_3 17%-Ni/15%-La_2O_3/Al_2O_3 17%_Ni/15%MgO/Al_2O_3	3	1023	N/A	N/A	N/A	N/A	>90 >80 >90 >90 ~100 ~100 ~100	100 100 100 100 100 100 100	N/A
[81]	Catalytic Acetic acid	3%-Ni/γ-Al_2O_3 9%-Ni/γ-Al_2O_3 12%-Ni/γ-Al_2O_3	4	873	14	N/A	24	30 >25 >26	N/A	>35 >45 >50	N/A

		15%-Ni/γ-Al_2O_3						>26		>45	
[126]	Catalytic Acetic acid	20%-Ni/Al_2O_3 20%-Co/Al_2O_3 20%-Fe/Al_2O_3 20%-Cu/Al_2O_3	15	873	N/A	24	N/A	N/A	N/A	100 100 >55 >60	>90 >90 ~30 >32
[86]	Catalytic Pine oil derv bio oil	18%- NiO/Al_2O_3	2.3[a]	873	18	N/A	N/A	1.2[b]	84[b]	>90[b]	N/A
	Palm empty fruit bunches bio oil	18%- NiO/Al_2O_3		873	18			1.3[b]	91[b]	81[b]	N/A
[87]	Catalytic Acetic acid	1%-Rh/Al_2O_3 1%-Pt/Al_2O_3 1%-Pd/Al_2O_3 1%-Rh/$Ce_{0.5}Zr_{0.5}O_2$ 1%-Pt/$Ce_{0.5}Zr_{0.5}O_2$ 1%-Pd /$Ce_{0.5}Zr_{0.5}O_2$	2	1035 1044 1019 1033 990 997	14	N/A	N/A	>70 >30 >25 >65 >60 >25	N/A	N/A	N/A

a- S/C ratio, b- Performance of the process of first cycle of chemical looping reforming

	Table 5

		Conditions			Definition			Reported values			
References	Catalytic/ Thermodynamic investigation	Catalyst	Steam/carbon(S/C)	\ Temp (K)	Yield Y (%)	Selectivity S (%)	Molar comp M_p (%)	Y (%)	S (%)	Conversion (%) -EQ 21	M_p (%)
[91]	Thermodynamic		5	573–1273	19	N/A	N/A	93	N/A	100	N/A
[94]	Catalyst Sunflower oil	Ni-Al catalyst with Ni/Al=2	9	826	N/A	N/A		N/A	N/A	100	71.7
[92]	Catalytic Waste cooking oil	18%- NiO/Al_2O_3	4	873	N/A	19	20	N/A	N/A	89	64
[93]	Catalytic Waste cooking oil	18%- NiO/Al_2O_3 catalyst dolomite	4 4	873 873	N/A	N/A	20	N/A	N/A	46	69.7
.[97]	Catalytic Palmitic acid Oleic acid Linoleic acid	$Ce-ZrO_2$ $Ce-ZrO_2$ $Ce-ZrO_2$		1173 1173 1173	N/A	N/A		N/A	71.8 69.2 67.4	100 100 100	71.8 69.2 67.4
[111]	FAME of soybean oil	Thermodynamic	0.66	573-873 K	23	N/A		76.97			57.24

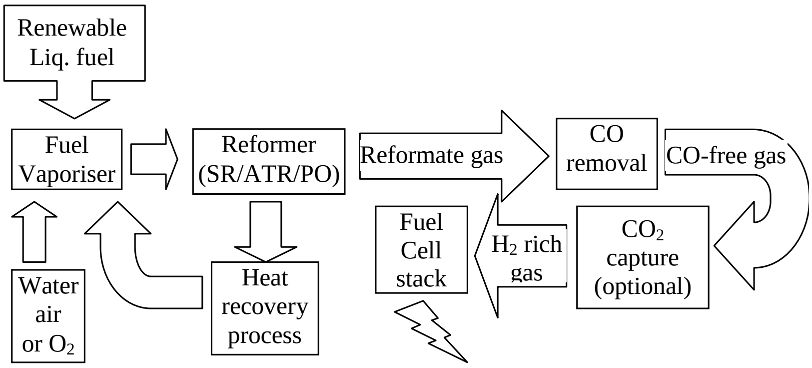

Figure 1: Schematic representation of a fuel processor for on board reforming to be used for fuel cell powered vehicles.

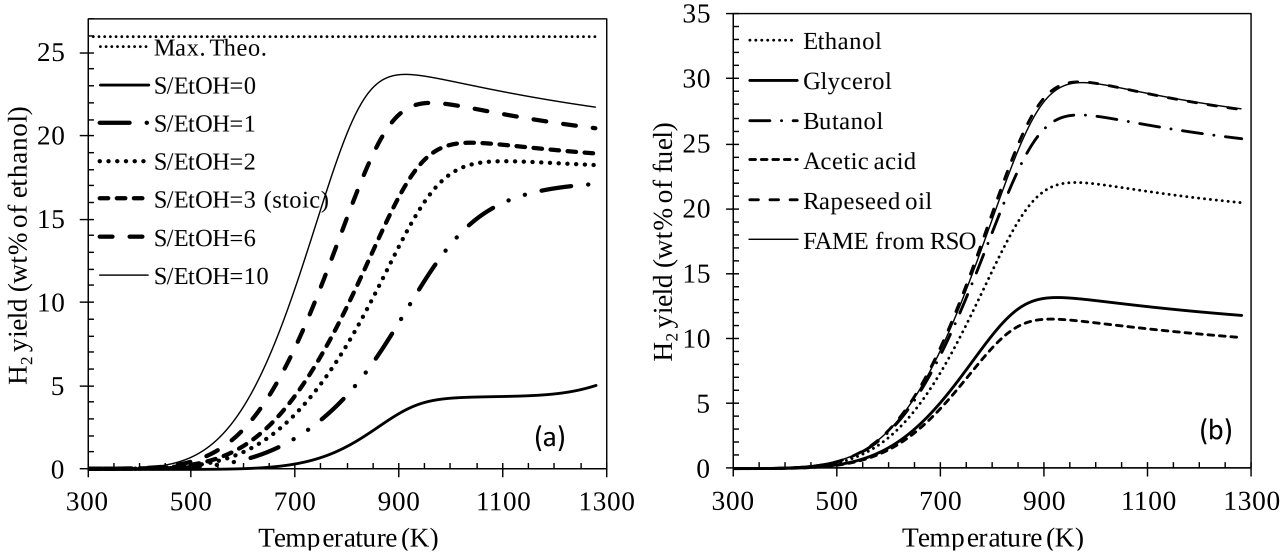

Figure 2 H_2 yield (in wt% of fuel) as function of temperature obtained by thermodynamic equilibrium calculations with a mol fraction of Ar of 0.2 and at 1 atm. (a) from SRE for various molar steam to ethanol ratio, Maximum theoretical is 26 wt%. (b) from SR of the fuels reviewed, at molar steam to carbon ratio of 3, Ar of 0.2 mol fraction, 1 atm. Acetic acid is included as a model compound of bio-oil, calculation procedure described in [92].

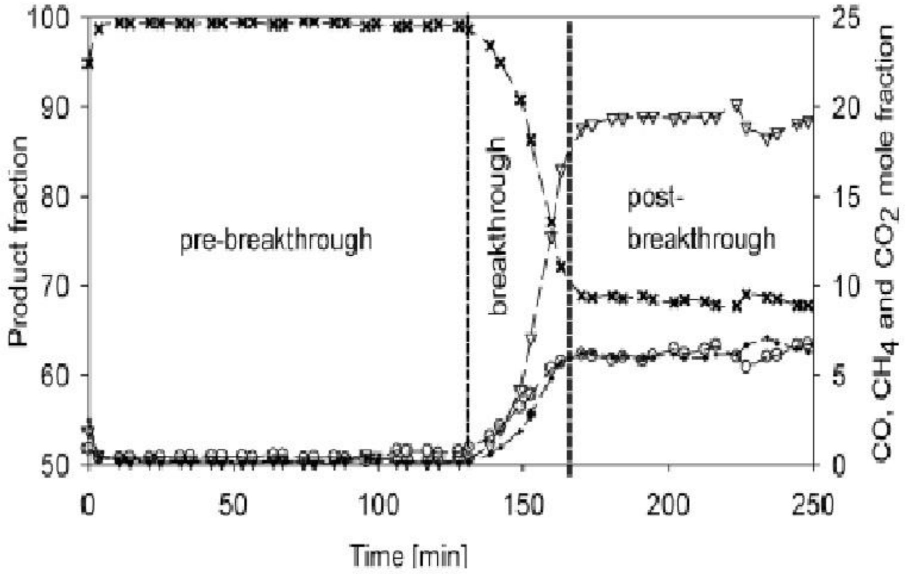

Figure 3: Effluent gas composition evolution in the reactions of the sorption enhanced SRE at a temperature of 823 K with an S/EtOH of 6 over a mixture of dolomite (10 g) and 40Ni/HTls (2 g) catalyst, ×-H_2, ▼-CO_2 and CH_4 and CO presented by o[26].

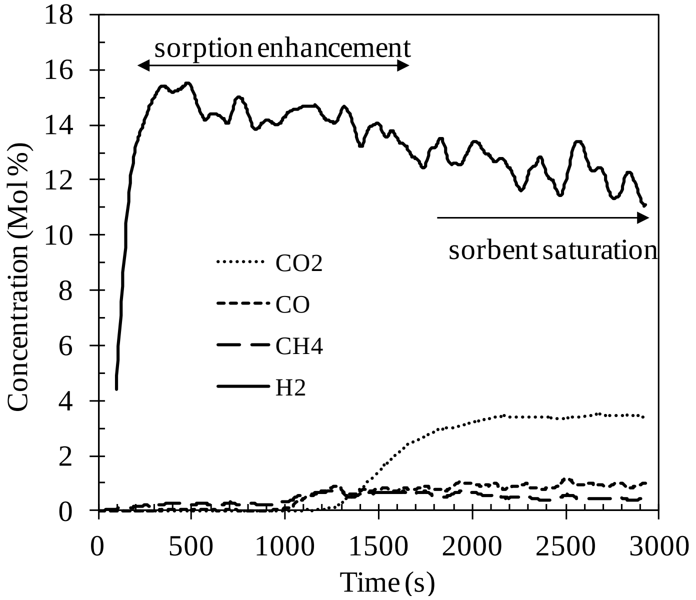

Figure 4: Species concentrations with time on stream during steam SR of crude glycerol with in-situ CO_2 capture, leading to sorption enhancement (nearly pure H_2 output with larger yield) prior to sorbent saturation. Reactor bed: 5 g of 18 wt%/Al_2O_3 catalyst mixed with 5 g of calcined dolomite, molar steam to carbon ratio of 3, temperature of 500 °C, weight hourly space velocity (WHSV) of 2.67 h^{-1}. Experimental set-up and fuel characteristics as in [51].

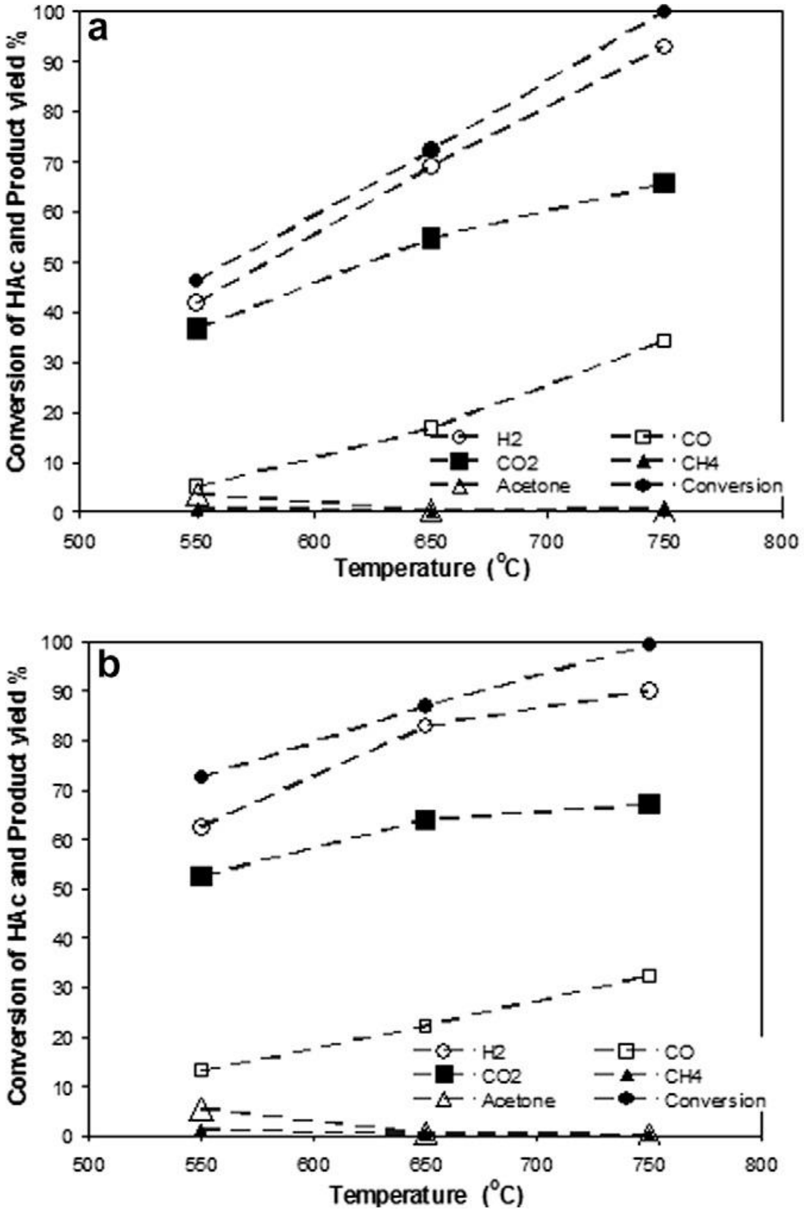

Figure 5: Effect of temperature on conversion and yield products over (a) Ni and (b) Rh catalysts supported on ceria–zirconia supports in SRA with S/A of 6[83].

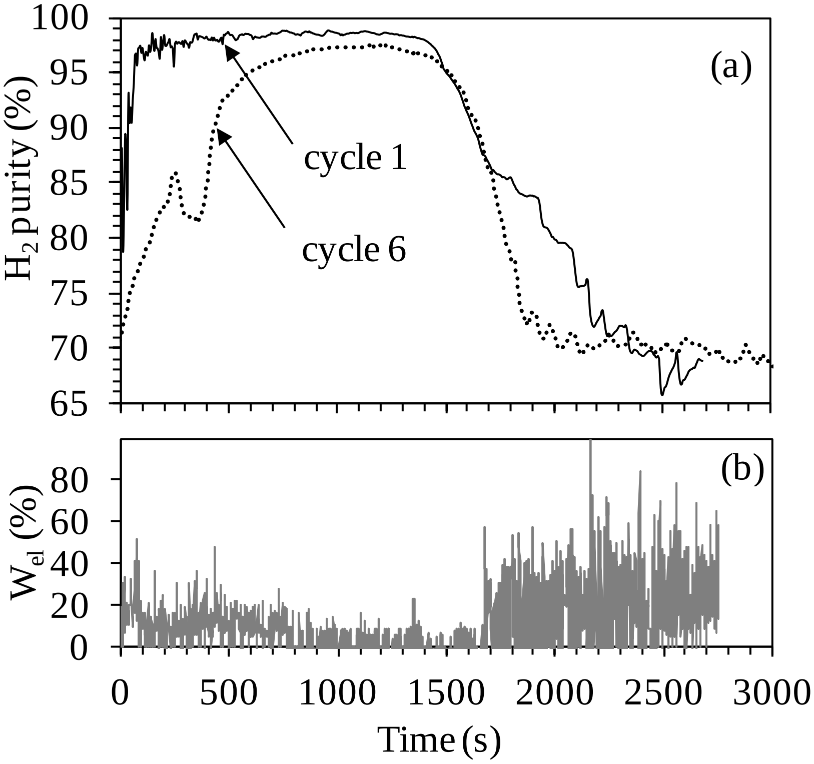

Figure 6: (a) Hydrogen purity (vol %) with time on stream during cycles 1 and 6 of sorption enhanced chemical looping steam reforming of waste vegetable oil in a packed bed reactor. (b) electrical power input to the reactor during cycle 1. Reactor bed: 40g of 18 wt% NiO/Al_2O_3 catalyst with 40 g of calcined dolomite. Steam to carbon molar ratio of 4, reactor temperature 873 K. The experimental set up is described in [93].

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The thermodynamic conditions obtained in this investigations can be used for the catalytic investigations.