

# Catalytic Reforming of Oxygenated Hydrocarbons for the Hydrogen Production: An outlook

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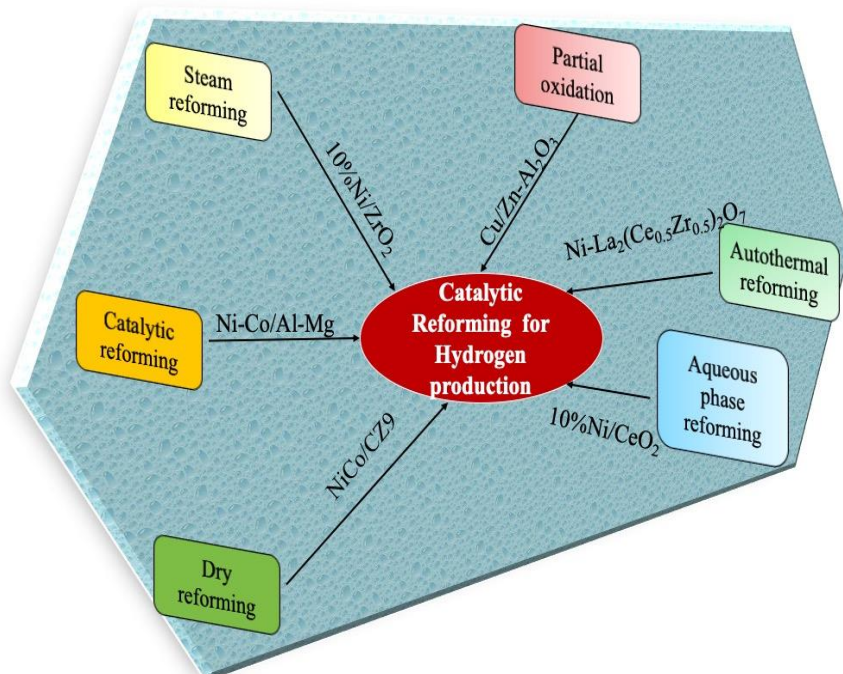
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## Graphical Abstract



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## 18 **Abstract**

19 The catalytic steam reforming of oxygenated hydrocarbons has been holding an interest for scientific societies for  
20 the past two decades. The hydrogen production from steam reforming of glycerol, ethanol and other oxygenates  
21 such as ethylene glycol and propylene glycol are more suitable choice not just because it can be produced from  
22 renewable sources, but it also helps to decrease the transportation fuel price and making it more competitive. In  
23 addition, hydrogen itself is a green fuel for transportation sector. The studies on the production of hydrogen from  
24 various reforming technologies revealed a remarkable impact on the environmental and socio-economic issues.  
25 Researchers became more focused on glycerol steam reforming (GSR), ethanol steam reforming (ESR) and other  
26 oxygenates to investigate the catalysts suitability, their kinetics and challenges for sustainability of the oil and gas  
27 production. In the present work, the authors critically addressed the challenges and strategies for hydrogen  
28 production via GSR, ESR and other oxygenates reforming process. This review covers extensively  
29 thermodynamic parametric analysis, catalysts developments, kinetics, and advancement in operational process for  
30 glycerol, ethanol and few other oxygenates. This detailed investigation only highlights the steam reforming  
31 process (SRP) of these oxygenates at laboratory experimental stage. It was found that from this review, there are  
32 many technical issues, which lead to economic challenges. The issues are yet to be addressed and thus these  
33 particular applications require faster accelerations at pilot scale, taking into the consideration of the current  
34 pandemic and economic issues, for a safer and greener environment.

35 **Keywords:** steam reforming; hydrogen production; catalysts; oxygenated hydrocarbons, partial oxidation.

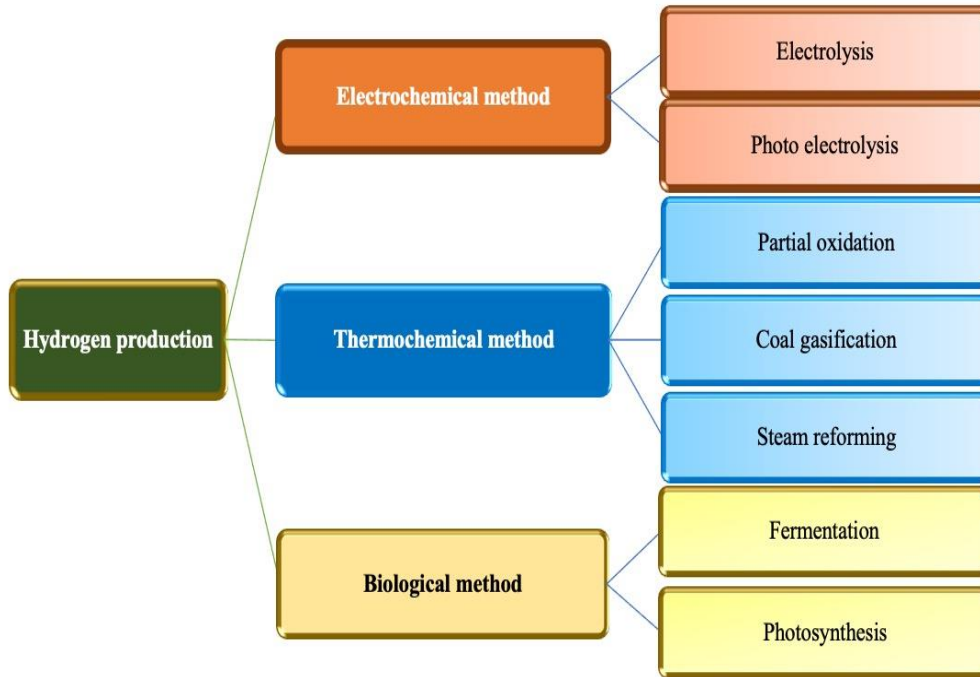
## 36 **1. Introduction**

37 The pursuit for a greener environment and struggle to reduce the dependency on fossil fuels has driven  
38 mankind to devise better energy solutions. Some of the effective solutions to combat the problem of fossil fuel  
39 dependency are the introduction of renewable energy, such as solar energy, wind power and biomass. Extensive  
40 research has proven that renewable energy not only extends the shelf life of the exhausting non-renewable fossil  
41 fuel but also reduces the level of carbon dioxide in the earth's atmosphere. In the year 2020 while more than 2/3  
42 of the world population are fighting with COVID-19, there are some good news with regards to the CO<sub>2</sub> emission  
43 from the industry. It is expected that there will be a drop in CO<sub>2</sub> emission from 4 to 11 % in 2020 [1], but this  
44 drop would not be sustainable. Over the next few years, if the governments do not take serious action now, it may  
45 overshoot as the trade and industries are trying to fulfil the previous demand or trying to justify continuing any

46 cancelled CO<sub>2</sub>-released projects in the past with the reason of relieving the economy. It is also important to provide  
47 green stimulus to the renewable energy companies to provide better technology that safeguarding our environment  
48 further, without further damaging the economy.

49           Nevertheless, the problems related to renewable energy sources, however, are still persistent. The sources  
50 are generally located at some specific locations. Although they are readily available, these sources are intermittent,  
51 such as solar and wind energy, and therefore unstable[2]. The International Energy Agency (IEA) predicts an  
52 increasing share of primary energy used from renewables in the future due to support from the government, the  
53 falling costs of renewable energy, change in the price of CO<sub>2</sub> emissions in certain regions and the rising price of  
54 fossil fuels in the long-term. Due to COVID-19 itself that is considered a blessing in disguise to the world  
55 environment, the only right thing needed by the governments is to ensure that CO<sub>2</sub> and other harmful gases  
56 released by the fossil fuels to continue decrease, and therefore their responsibility is to stick by the earlier plan to  
57 ensure the renewables will be continued to be supported despite a shortfall of the fossil fuel prices.

58           One possible greener energy solution in the future is the utilization of hydrogen, which is always known  
59 as the energy carrier since the hydrogen atom cannot exist on its own. Hydrogen has been identified as an ideal,  
60 sustainable energy carrier due to its abundance and high energy density [3]. Conventionally, it is produced from  
61 natural gas reforming and coal gasification. Approximately 96% of world hydrogen comes from fossil fuels [4].  
62 Utilizing hydrogen as an energy carrier in the future is very beneficial as it preserves the environment, is  
63 economical and can be safely handled [5]. Figure 1 shows the hydrogen production through various methods such  
64 as electrochemical, thermochemical and biological methods using various feedstocks.



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**Fig. 1.** Hydrogen production using various methods.

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Prior to the consumption of hydrogen for the fuel cell and transportation era, large amounts of hydrogen were used as a feedstock for other chemical productions. Hydrogen is consumed in ammonia production, petroleum refining industry and methanol production [6]. Hydrogen for petrochemical utilization came in fourth place in which hydrogenolysis and hydrogenation account for most of the hydrogen consumed in this industry. This is provided on a large-scale from the steam reforming of natural gas as well as the by-product of petroleum refining and chemical production, mainly from the catalytic reforming process [7]. In nature, natural gas is not sustainable; therefore, the utilization of alternative fuels, such as oxygenated hydrocarbons from biomass, is not only a sustainable source but can be found in abundance. These biomasses can be transformed into different fuels in solid, liquid or gas forms by applying different technologies, namely, pyrolysis, gasification, reforming, and other bio-based processes[8,9].

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The International Energy Agency (IEA) reported that hydrogen should now be given an important role as it is impacting the economic potential of the world. Therefore, as reported in 2019 Fuel Technologies Report, it is imperative now to consider a major preparation towards hydrogen utilization [10]. Additionally, due to the unprecedented scenario in 2020, it has to be done right from the re-start point i.e. post COVID-19. Hydrogen as a greener fuel should be utilized worldwide with the strong lobby to the governments. Several researchers estimated

82 that clean hydrogen production is cost effective when it is widely installed. However, according to some other  
83 estimation, the cost of the hydrogen production may not dawn until 2030s. Nevertheless, despite of its current  
84 high cost, our future can be surrounded with clean hydrogen that would be affordable soon, which is mainly  
85 dependent the source of hydrogen come from.

86 Presently, hydrogen is mainly produced from industrial natural gas, which is mainly responsible for CO<sub>2</sub>  
87 emission known as “grey hydrogen”. Another cleaner version of hydrogen is “blue hydrogen”, of which the  
88 hydrogen is generated from carbon emission captured, stored and reused. Among all cleaner hydrogen, “green  
89 hydrogen” is the cleanest form of hydrogen produced from renewable sources without emitting CO<sub>2</sub>. Currently,  
90 grey hydrogen is inexpensive than other two types. However, the increase of the carbon footprint cannot be  
91 ignored and to be accepted as a norm. In contrast, the price of blue hydrogen is mainly depending on natural gas  
92 price besides the carbon capture store and reuse cost. In present scenario, blue hydrogen is pricier than grey  
93 hydrogen in Europe, but it is expected that the price will reduce if the price of CO<sub>2</sub> emission increases in the  
94 future. Furthermore, when the process of carbon capture is used, and storage process is scaled up, the blue  
95 hydrogen will be cheaper.

96 For the production cost of green hydrogen, there are several factors, which influence the process cost.  
97 One of them is electrolysis process cost using water as renewable energy source. The global electrolysis capability  
98 is inadequate as well as it is still expensive in nature. It is reported in IEA 2019 report that most of the industrial  
99 experts are expecting that the electrolysis capacity will significantly decrease in future and will reduce the cost  
100 down to 70%, to be the same as the cost of solar and wind energy, which has come down during the past decade.

101 Reforming is a well-developed thermal technology in which the desired product is mainly hydrogen (H<sub>2</sub>)  
102 with carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO) and methane (CH<sub>4</sub>) being the usual side products. This could  
103 be considered as the ‘blue’ hydrogen technology as the reforming process is still releasing the CO<sub>2</sub>, but it is a  
104 derivative from the plants and biomass, and hence the CO<sub>2</sub> released shall revolve in its own cycle. The reformer’s  
105 effluents can be varied either thermodynamically or by using different types of catalysts to obtain a high yield of  
106 H<sub>2</sub> or syngas. To date, many reforming processes utilizing oxygenated hydrocarbons have been researched.  
107 Several reviews has been reported on various technologies [11,12]. These include dry gas reforming, also known  
108 as CO<sub>2</sub> reforming, steam reforming, hydrothermal reforming (also known as aqueous phase reforming), partial  
109 oxidation and autothermal reforming [13-15]. Among the growing interests of oxygenated hydrocarbons  
110 undergoing reforming technologies are the short chain alcohols (monohydric alcohols), such as methanol and

111 ethanol (or bio-ethanol) [16], and polyhydric alcohols, such as glycerol [17,18]. The biomass oil (bio-oil), which  
112 is obtained via pyrolysis activity, may also be used to undergo the reforming process, however, the bio-oil consists  
113 of a more complex mixture that may include aldehydes, ketones and carboxylic acids [19-21]. Most of these  
114 mentioned oxygenates can be obtained from biomass derivative products [22,23]. Glycerol ( $C_3H_8O_3$ ), as an  
115 example, is a by-product of biodiesel production [23,24]. Glycerol is widely used in many applications including  
116 personal care, food, oral care, tobacco, polymer and pharmaceutical applications. However, the crude glycerol  
117 that is obtained from biodiesel production has to undergo an energy intensive distillation process to purify glycerol  
118 to an acceptable purity, which is costly [23]. Avasthi et al. [24] reported that, at the moment, biodiesel production  
119 is costlier than the petroleum diesel, and that one of the ways to reduce the cost is to utilize the by-product  
120 (glycerol) effectively, which is further supported by Quispe et al. [25].

121           There are still many challenges that have not been fully addressed in catalysis and reaction engineering  
122 of oxygenates, such as the most effective reformer design, its performance efficiency as well as the catalyst  
123 development. In terms of the technical aspects, among the challenges that are yet to be tackled at this stage include  
124 the deactivation, resulting from coking of the catalyst, metal sintering of the catalysts at high temperature, high  
125  $CH_4$  selectivity that leads to difficulties in product separation and non-ideal reactors. Other challenges may  
126 comprise determining the mechanisms and kinetics of the process as well as intensifying the conventional  
127 technology to accelerate the hydrogen production. Although some of the catalysts may give high yield and  
128 selectivity of the desired products, the cost may be expensive and unfeasible to be utilized on an industrial scale.

129           This comprehensive review will provide a broad view of the previous works carried out by other  
130 researchers focusing on oxygenated hydrocarbons of choice, reforming technologies, thermodynamic analyses of  
131 respective reforming technologies, catalyst and reactor development associated with reforming reactions, and,  
132 finally, the challenges in the reforming of oxygenated hydrocarbons.

## 133 **2. Reforming Technologies**

134           Reforming is a well-developed technology for converting hydrocarbon into molecular hydrogen, and  
135 carbon dioxide or syngas (hydrogen and carbon monoxide) at a high temperature of usually between 400 to 800°C.  
136 Generally, several main reactions occur during the reforming process. However, it is vital to be aware that  
137 reforming technology is highly dependent on the type of reactant used during the process. Hydrogen ( $H_2$ ) and  
138 carbon dioxide ( $CO_2$ ) are normally released as the main products of a full reactant conversion. However, there are

139 times that carbon monoxide (CO) and methane (CH<sub>4</sub>) may also be produced during the process. To date,  
140 considerable reforming research and developments have been implemented. These include steam reforming, dry  
141 gas reforming, also known as CO<sub>2</sub> reforming, hydrothermal reforming (also known as aqueous phase reforming),  
142 partial oxidation and autothermal reforming. Fig. 2 illustrates the overview of reforming technologies and catalyst  
143 development, focused in this review.

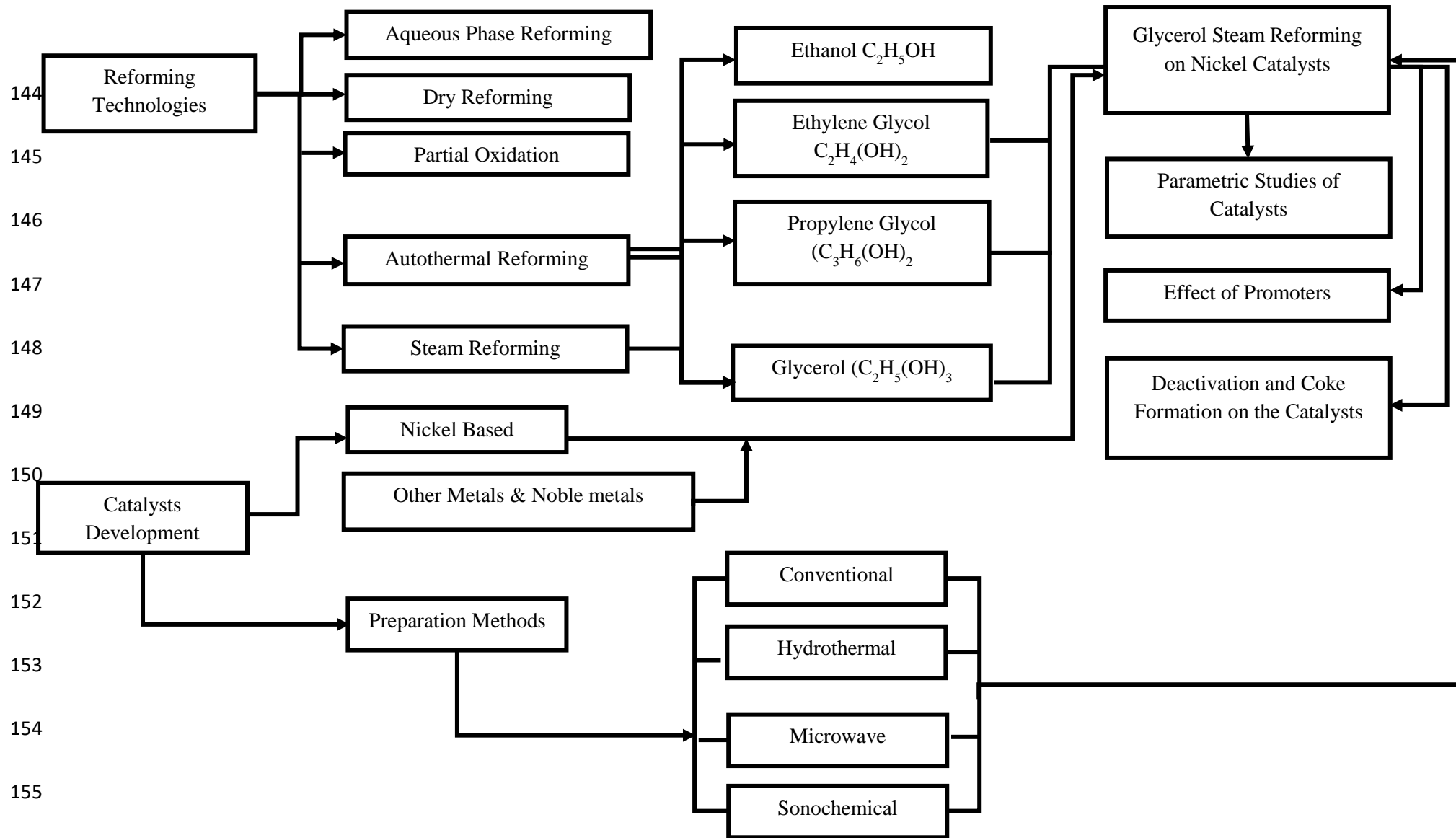


Fig. 2. The overview of reforming technologies, catalysts and its applications.



## 2.1. Oxygenates for Reforming Technologies

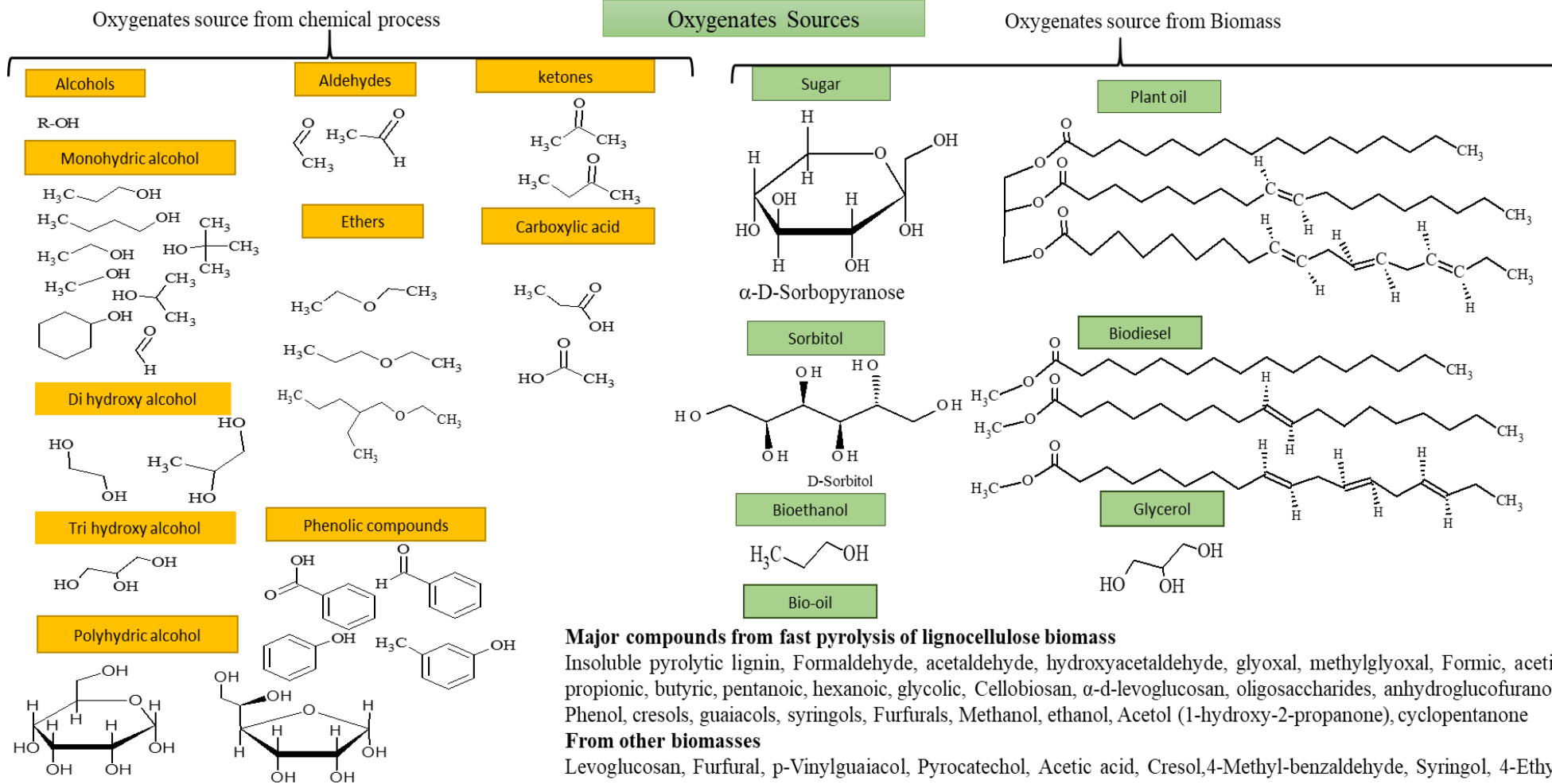
Oxygenated hydrocarbons are considered to be one of the potential sources of fuel for the reforming technology to complement the utilization of natural gas (methane) [26]. The growing interest in oxygenated hydrocarbons includes the short chain alcohols (monohydric alcohols), such as methanol and ethanol (or bioethanol), and polyhydric alcohols, such as glycerol, due to their availability from bio-derivative resources, which means that they can be sustainably produced [27]. The biomass oil (bio-oil), which is obtained via pyrolysis of lignocellulosic biomass, may also be reformed [28]. The bio-oil may include water, lignin fragments, aldehydes, carboxylic acids, carbohydrates, phenols, furfurals, alcohols, and ketones; however, the reactions involved are complex and may lead to deactivation via coking of the catalyst [29]. For the purpose of this review, particular attention is focused on four main alcohols forming a series of poly-ols homologues: ethanol (mono-ol), ethylene glycol and propylene glycol (1,2-propane diol) forming di-ols and glycerol (tri-ols) and some other oxygenates such as acetone, acetic acid and phenols. Fig. 3 shows commonly used oxygenates produced through chemical process and biomass for reforming technologies reported in various literatures.

Since the steam reforming process is an endothermic process, which requires high temperature [30], it is highly beneficial to use oxygenated hydrocarbons as the fuel source to complement the amount of heat used, and, ultimately, save the heating cost. Among the alcohols that are beneficial for reforming is ethanol. Ethanol ( $C_2H_5OH$ ) has a relatively high hydrogen content, is widely available, non-toxic and can be stored and handled safely [13]. Several researches have been conducted for hydrogen production using ethanol and methanol or polyhydric alcohols. For example, Hou et al. [31] stated in his review on steam reforming of ethanol that the production of hydrogen from ethanol is considered as most favorable technique for renewable and sustainable energy development. Moreover, operating conditions, the production yield of hydrogen mainly depends on nature of catalysts selected.

Glycerol is one of the potentials oxygenates for reforming techniques to produce hydrogen. Recently, with the increased production of biodiesel, a surplus of glycerol is expected in the world market, and, therefore, it is essential to find useful applications for glycerol [24]. At present, most of the crude glycerol obtained from biodiesel plants is sent to water treatment for digestion, however, this process is slow, expensive and has low yield. By observing the current condition, it is obvious that there is a major need to find an alternative use for glycerol.

188 Another two more components that are of interest are ethylene glycol ( $C_2H_6O_2$ ) and 1,2-propane diol  
189 ( $C_3H_8O_2$ ), also known as propylene glycol. These polyols are part of the glycerol building block. At the industrial  
190 scale currently, the widely used method of ethylene glycol production is via non-catalytic thermal hydrolysis of  
191 ethylene oxide, which is a product of the direct oxidation of ethylene in air or oxygen. Propylene glycol has a  
192 similar property to ethylene glycol, as reported by Sullivan [32]. In addition, propylene glycol is readily  
193 biodegradable. Sullivan further adds that direct hydrolysis of propylene oxide with water is the only practical and  
194 industrially accepted method for propylene glycol production.

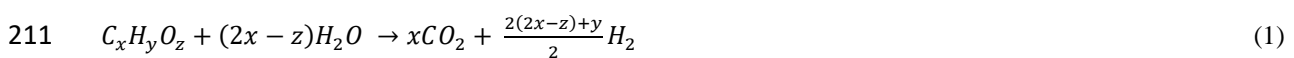
195 Acetone is produced through cumene process which produced phenol and acetone as the desired products  
196 [33]. Approximately one mole of acetone is produced for one mole of phenol. The demand of phenol in industry  
197 lead to higher production of phenol as well as acetone. Therefore, extensive research should be done to convert  
198 acetone into valuable gas and liquid products. Acetic acid is the simplest carboxylic acid produced from  
199 homogeneous catalytic carbonylation of methanol under mild operating conditions [34]. A recent research has  
200 been reported on catalytic reforming of wood vinegar, which shows high hydrogen production over Ni based  
201 catalysts [35].



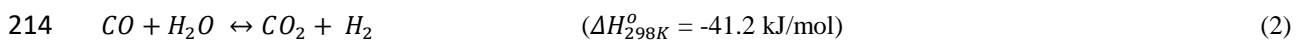
## 204            **2.2. Steam Reforming**

205            Steam reforming is the most common and deep-rooted reforming technology and is well developed in  
206 the petrochemical industry to convert natural gas (mainly methane) into hydrogen. This reaction is endothermic  
207 in nature. Many research works have focused on improving the performance of this technology using other  
208 hydrocarbons, e.g. oxygenated hydrocarbons (e.g. methanol, ethanol, glycerol, dimethyl ether, acetone and acetic  
209 acid) or heavier hydrocarbons (C<sub>3</sub> – C<sub>10</sub> components).

210 For oxygenated hydrocarbons, the stoichiometric reaction mechanism is as follows:



212 In a complete conversion of an oxygenated hydrocarbon, the reforming reaction is normally accompanied by a  
213 water gas shift reaction, as follows:



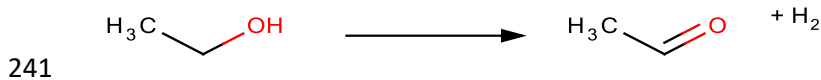
215 Steam reforming is usually carried out at high temperature (400 – 800°C) and atmospheric pressure, but,  
216 sometimes, at elevated pressure for industrial practice [36]. The operating temperature depends on the type of  
217 reactants of which higher hydrocarbon chains would require a higher reaction temperature for better conversion.  
218 Nonetheless, this is limited to the ability of the catalyst (usually a metal catalyst) to withstand the temperature  
219 from sintering. Although this technology is highly preferred since it is an established technology with minimum  
220 by-products, this process requires intensive energy input to sustain the operating temperature.

221            The parametric effect of reforming conditions such as temperature, space velocity, steam/biomass ratio  
222 play an important role in catalytic process of steam reforming of biomass. In addition, the challenges of this  
223 technology are often associated with catalyst deactivation resulting from metal sintering at high temperature as  
224 well as coking, which is also linked with thermodynamic limitations and catalyst activity. For most of the  
225 oxygenated hydrocarbons, it is common to have a lower hydrogen selectivity, which is associated with  
226 decomposition of components at high temperature, dehydration resulting from insufficient steam and  
227 dehydrogenation. These side reactions may lead to the formation of alkanes, alkenes, aldehydes and ketones, for  
228 which coke may finally form on the catalyst surface, hence contributing to catalyst deactivation. Table 1. Illustrate  
229 the glycerol steam reforming (GSR) using various catalysts and their optimized conditions.

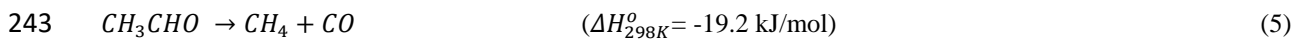
230 Taking ethanol as an example of oxygenated hydrocarbons for steam reforming reaction will generally  
 231 follow this stoichiometric reaction:



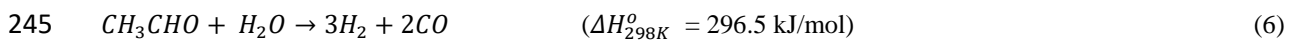
233 However, this is not a straightforward reaction as there are several intermediates formed during this  
 234 process depending on the catalyst used and the thermodynamic properties. Casanovas et al. [37] and Zhang et al.  
 235 [38] reported that during the reforming process, ethanol is highly favored to undergo ethanol dehydrogenation,  
 236 which forms acetaldehyde as the reaction intermediate. This is possible since dehydrogenation of ethanol, even  
 237 though it is an endothermic reaction, is at a lower magnitude compared to the endothermic steam reforming  
 238 process, and thus the choice of catalyst is highly crucial to route the reaction to the desired products.  
 239 Dehydrogenation of ethanol follows this stoichiometric reaction [39]:



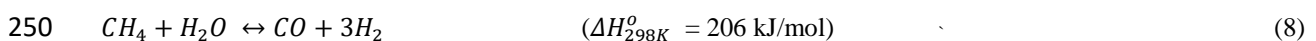
242 Acetaldehyde undergoes decomposition to methane and carbon monoxide, respectively:



244 Otherwise, acetaldehyde may undergo steam reforming, as follows:

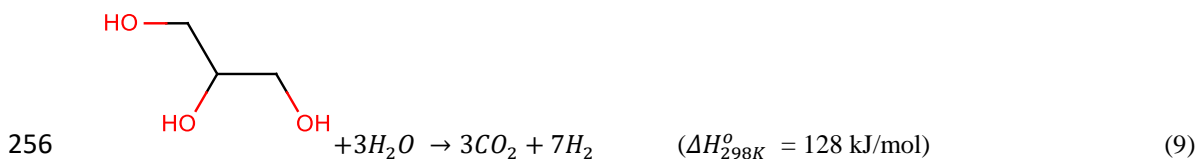


246 If reaction (5) has high methane selectivity, eventually, CH<sub>4</sub> will undergo steam reforming to produce hydrogen  
 247 with CO<sub>2</sub> and/or CO, as shown in equations 7 and 8. CO will further undergo water gas shift reaction (WGS) to  
 248 produce CO<sub>2</sub> and H<sub>2</sub>, as shown earlier in equation (2).



251 The temperature range for operating ethanol steam reforming is quite wide, ranging from 300 – 650°C  
 252 [40-42,38]. With the presence of a catalyst, it is possible to achieve complete conversion of ethanol at 350°C and  
 253 at atmospheric pressure, whilst a non-catalytic reaction may require a higher temperature for a complete

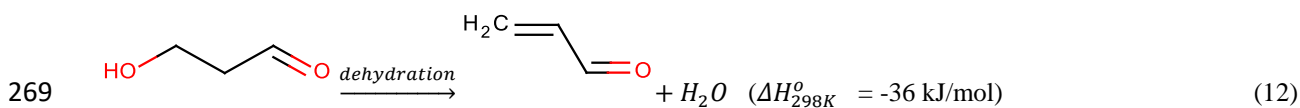
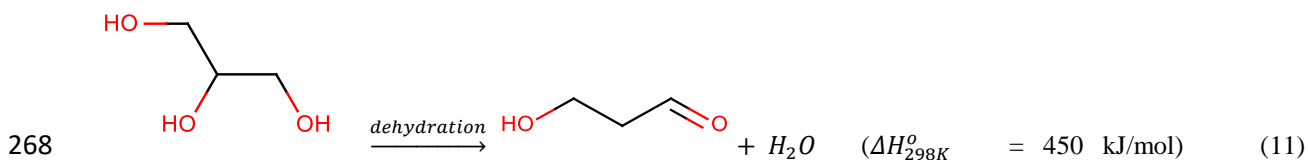
254 conversion [42]. Glycerol steam reforming research work has been reported by many researchers [43-46] in last  
 255 decades. Glycerol steam reforming follows this stoichiometric reaction:



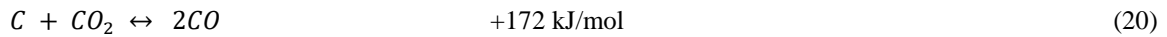
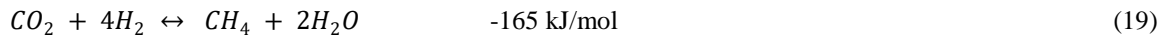
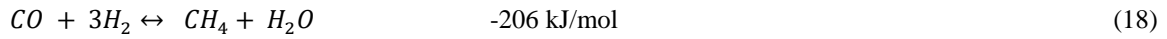
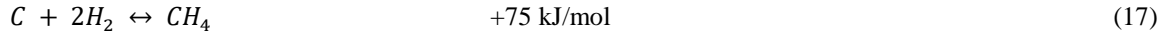
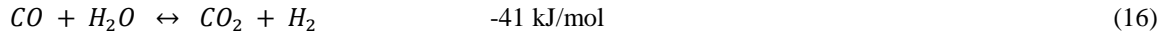
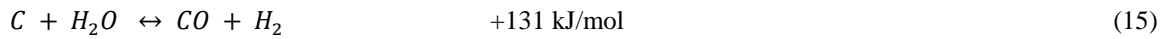
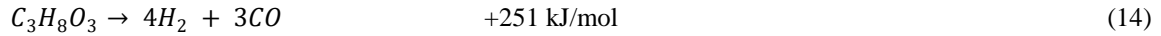
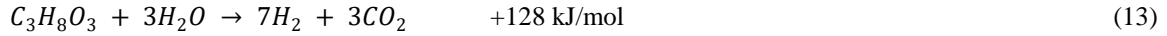
257  
 258 There are a few possible routes of reactions, depending on the type of catalyst and conditions provided  
 259 to the system, e.g. enough steam to fuel ratio as well as operating temperature. However, most of the research  
 260 works reported that glycerol decomposed into acetaldehyde, propanal, acetone, acrolein and other short chain  
 261 alcohols, resulting from competing dehydration and dehydrogenation [47]. Chiodo et al. [48], however, reported  
 262 that glycerol underwent the phenomenon of pyrolysis at high temperature in which it was decomposed into  
 263 primary and secondary pyrolysis products prior to reaching the catalyst surface. Thus, reaction (2), (8) and glycerol  
 264 decomposition, as shown in equation (10), may occur apart from the glycerol steam reforming reaction:



266 Other possible decomposition reaction resulting from dehydration of glycerol to 3-hydroxypropanal, which  
 267 becomes the precursor of acrolein formation [49]:



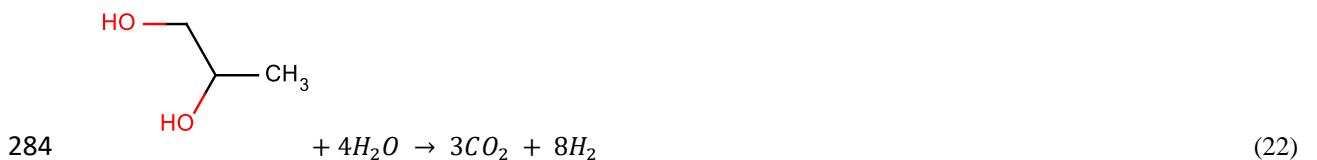
270 Slinn et al. [50] demonstrated that steam reforming of pure glycerol and raw glycerol from a biodiesel  
 271 plant produces hydrogen. The reaction pathways, as adapted from  
 272 Sutton et al. [51], are shown as follows with the respective reaction enthalpy ( $\Delta H_{298K}^0$ ):



273 Recently, glycerol steam reforming has been researched under supercritical water conditions with or  
 274 without the presence of a catalyst [52-58]. Markočić et al. [56], in their review article, explained that supercritical  
 275 water condition means the operating pressure and the temperature exceeds the water critical point, i.e.  $T_c = 647 \text{ K}$   
 276 ( $274^\circ\text{C}$ ) and  $P_c = 221 \text{ bars}$ . They highlighted several researches works conducted earlier in which supercritical  
 277 water reforming of glycerol may yield lighter molecular weight aqueous phase hydrocarbons and gases within the  
 278 temperature range of 300 to  $600^\circ\text{C}$ . Most of the work reported the presence of acrolein and acetaldehyde, apart  
 279 from the production of hydrogen,  $CO_2$ ,  $CO$ , and other  $C_xH_y$  gases.



281 To date, in respect of propylene glycol, although none of the work mentioned above covered propylene  
 282 glycol steam reforming or other reforming technologies, it is a possible reaction with the following theoretical  
 283 stoichiometric equation:



285 The maximum hydrogen molecular yield possible to be achieved in propylene glycol steam reforming is  
 286  $2.67 \text{ mol/mol C}$ , which is higher than ethylene glycol ( $Y_{H_2} = 2.5$ ) and glycerol ( $Y_{H_2} = 2.33$ ), but relatively lower  
 287 than ethanol ( $Y_{H_2} = 3$ ). Propylene glycol however has been researched to be produced by glycerol, via

288 hydrogenolysis [59]. All four oxygenated hydrocarbons chosen to make up a series of homologues, which form  
289 an interesting set for investigation.

290 Hydrogen production through reforming technology has gained interests many of researches as this  
291 technology utilize oxygenated hydrocarbons such as ethanol, glycerol and acrolein which is produced as by-  
292 products in some industry as the raw materials. There are several reforming technologies studied which are steam  
293 reforming, dry reforming, aqueous phase reforming, partial oxidation and autothermal reforming. However, these  
294 reforming processes are prone to undergo other side reaction such as decomposition, dehydration and  
295 dehydrogenation which can cause coke formation and catalysts deactivation at high temperature. Therefore, the  
296 selection of the catalyst is very important to prevent catalyst deactivation and to ensure high selectivity of  
297 hydrogen. The thermodynamic properties such as steam to fuel ratio (steam reforming and APR), temperature and  
298 oxygen to carbon ratio (in autothermal reforming) also need to be considered for the processes. Steam reforming  
299 of oxygenated hydrocarbons is extensively studied by many researchers over the other reforming technologies as  
300 it is the most feasible reforming technology with high hydrogen selectivity and minimum production of by-  
301 products. Oxygenated hydrocarbons, mainly from polyol group has gain interest as there is oxygen atom present  
302 that weakens the C-C bonds which cause easier splitting between H and CO. A general reaction routes are  
303 represented for glycerol in Fig. 4. Based on the literature, it can be seen that ethanol and glycerol are the common  
304 polyols studied for the reforming technology. However, propylene glycol was less studied for the reforming  
305 technology.

306 Very few studies have been reported for steam reforming of acetone i.e. one of the major by-products of  
307 bio-oil. This might be due to very low boiling point and high vapor pressure. Recently, the study was performed  
308 by Elias et al. [60] investigated the Ni/ZnO/CeO<sub>2</sub> based catalysts for the steam reforming of acetone for the  
309 production of hydrogen. The study revealed that Ni/ZnO with in cooperation of CeO<sub>2</sub> performed better than barely  
310 Ni/ZnO. Elias et al. [60] particularly investigated in detail the carbon deposition and catalytic behavior.  
311 Ni/xCeZnO firstly produced low coke deposition compared to Ni/ZnO. Secondly, the increase of CeO<sub>2</sub> loading  
312 significantly increased the hydrogen production and changed the carbon nature from hard carbon to carbonaceous  
313 graphite.

314 Some other catalysts such as Mn, Fe, Ni, Co, Cu and Zn were investigated for aqueous phase reforming  
315 of acetic acid and acetone by Li et al. [61] recently. Based on Li et al. screening of different metal catalysts, it was  
316 reported that Mn, Fe and Zn based catalysts were not significantly active for steam reforming of acetone. This



317 result mainly due to low capacity of metals to break the C-O bond. According to Li et al. [61] findings, Co and  
318 Cu based catalysts were found to be more active only for methanol steam reforming rather than acetone. The main  
319 difference of catalytic activity of Co and Ni was also insignificant. Nonetheless, the reforming of acetone was  
320 comparatively more difficult than that of acetic acid due to large molecular size. The difference of catalytic  
321 behavior and physicochemical properties of transition metal catalysts should be considered carefully to use in  
322 steam reforming of other organic compounds such as acetone, acetic acid and methanol.

323 One of the remaining challenges in glycerol steam reforming is high conversion versus high selectivity  
324 towards hydrogen production. From Table 1, in general, high conversion of GSR over transition metal catalysts  
325 yield less hydrogen compared to noble metal catalysts or support other than alumina. The correlation can be built  
326 among the metal support and selectivity, low hydrogen yield and high conversion will lead the reaction to other  
327 side reactions or by products. High selectivity of hydrogen only can be achieved over activated carbon or modified  
328 alumina support under almost similar operating condition. The tabulated results from various literatures mainly  
329 focused on screening of catalysts under similar operating condition, which gives a comprehensive outcome to  
330 select the most suitable catalysts.

331 Suitable vaporization temperature prior to entering the main reactor must also be carefully selected, as  
332 high vaporization temperature would favor the glycerol to be decomposed first into other homogeneous reaction  
333 products such as ally alcohol, acetol and acrolein[62]. In addition to this, different type of promoters and supports  
334 would favor either hydrogenolysis, dehydrogenation, condensation, polymerization, hydrogenation or dehydration  
335 reactions, which can be explained from Fig. 4, using example of Ni-Ca/Al<sub>2</sub>O<sub>3</sub> catalyst. As such, GSR is a delicate  
336 process, for which the kinetics need to be investigated with care prior to any pilot studies or commercialization  
337 purposes. On top of these, the crude glycerol from the biodiesel production may contain a lot more impurities with  
338 inconsistent compositions and hence making the technology is much more challenging.

339

**Table 1.** Glycerol Steam Reforming (GSR) using various catalysts and their optimized conditions.

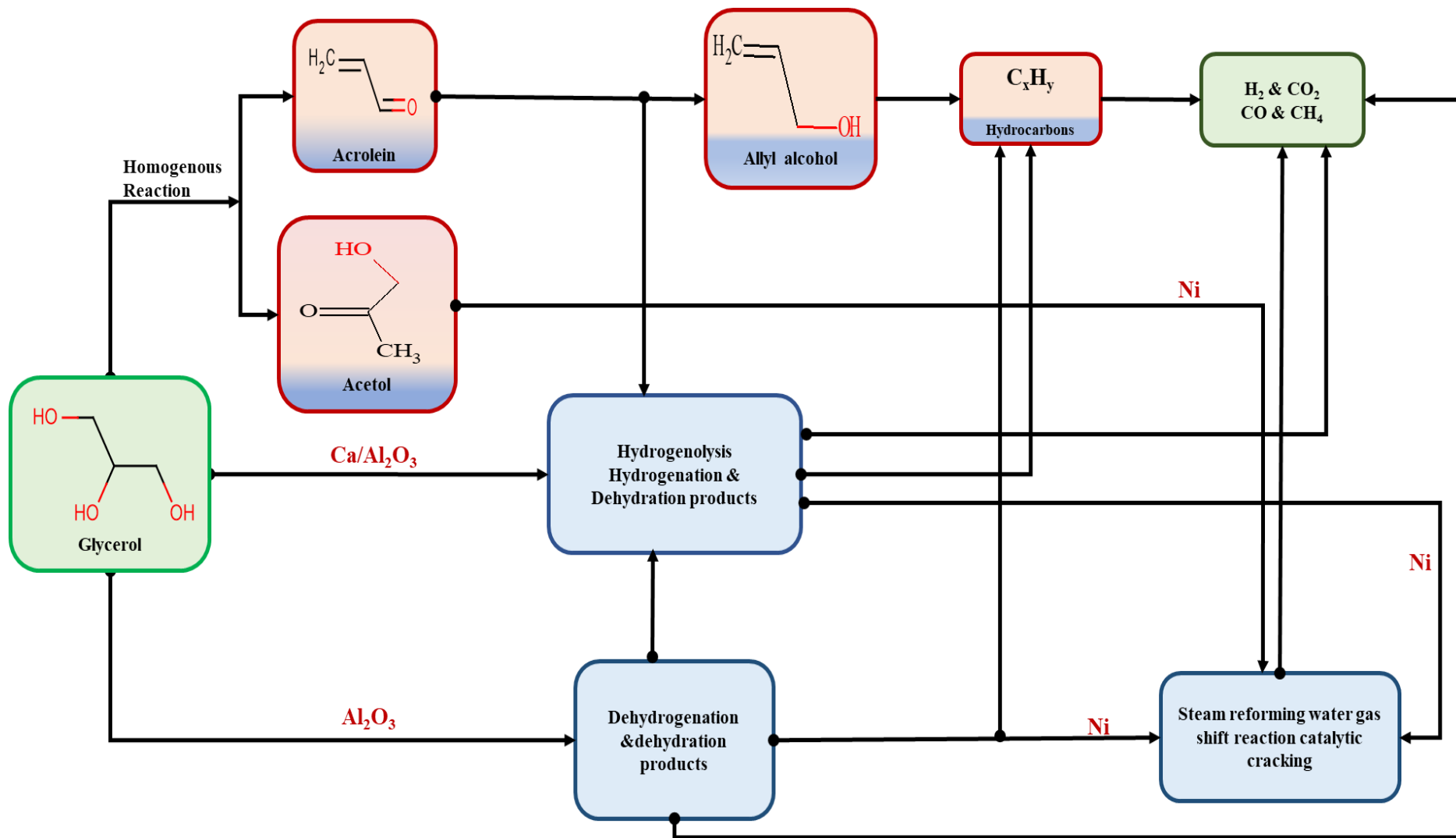
Catalyst	Operating Conditions			GSR		H Yield (%)	Ref
	T	P	FFR	WGFR (h)	Conversion		
	(°C)	(atm)	(mL min <sup>-1</sup> )	wt. % glycerol	%	%	
10 wt% Ni/ZrO <sub>2</sub>	650	1	0.06	10	72	65	[63]
10 wt% Ni/SiC	400	1	WHSV=33.3 h <sup>-1</sup>	9	95.2	NA	[64]
10 wt% Ni/Al	500	1	GHSV=0.95 min <sup>-1</sup>	W:	25	1.2	[65]
				G=3.5:1	62	2.6	
				W: G=6:1			
10 wt% Ni/Al	600	1	GHSV=0.95 min <sup>-1</sup>	W:	56	2.2	[65]
				G=3.5:1	84	3.6	
				W: G=6:1			
10 wt% Ni-3 wt% Mg/Al	500	1	GHSV=0.95 min <sup>-1</sup>	W:	40	1.8	[65]
				G=3.5:1	70	2.9	
				W: G=6:1			
10 wt% Ni-3 wt% Mg/Al	600	1	GHSV=0.95 min <sup>-1</sup>	W:	61	2.5	[65]
				G=3.5:1	92	4	
				W: G=6:1			
10 wt% Ni-5 wt% Mg/Al	500	1	GHSV=0.95 min <sup>-1</sup>	W:	32	1.4	[65]
				G=3.5:1	64	2.5	
				W: G=6:1			
10 wt% Ni-5 wt% Mg/Al	600	1	GHSV=0.95 min <sup>-1</sup>	W:	56	2.2	[65]
				G=3.5:1	82	3.8	
				W: G=6:1			
10 wt% Ni-10 wt% Mg/Al	500	1	GHSV=0.95 min <sup>-1</sup>	W:	26	1.2	[65]
				G=3.5:1	30	1.4	
				W: G=6:1			
10 wt% Ni-10 wt% Mg/Al	600	1	GHSV=0.95 min <sup>-1</sup>	W:	44	2	[65]
				G=3.5:1	78	3.4	

W: G=6:1							
Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	400- 600	1	W/F=1.05 mg min ml <sup>-1</sup>	20	42-90	22-80	[66]
Ni/B <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	400- 600	1	W/F=1.05 mg min ml <sup>-1</sup>	20	20-70	10-60	[66]
Ni/La <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	400- 600	1	W/F=1.05 mg min ml <sup>-1</sup>	20	72-92	46-70	[66]
Ni/Al	400- 750	1	0.12 WHSV=50000 mL g <sup>-1</sup> h <sup>-1</sup>	20	85-95	0.4-4.4	[67]
Ni/modAl	400- 750	1	0.12 WHSV=50000 mL g <sup>-1</sup> h <sup>-1</sup>	20	88-95	0.8-6	[67]
Ni/LaAl	450- 750	1	0.12 WHSV=50000 mL g <sup>-1</sup> h <sup>-1</sup>	20	18-90	5-50	[68]
Ni/AC	650	1	0.03	30	40	44	[69]
NiY/AC	650	1	0.03	30	30	80	[69]
NiLa/AC	650	1	0.03	30	70	80	[69]
NiMg/AC	650	1	0.03	30	85	85	[69]
Rh/NiMg/AC	650	1	0.03	30	82	90	[69]

341 ND: Not determined

342 WHSV: Weight hour space velocity

343 GHSV: gas hour space velocity

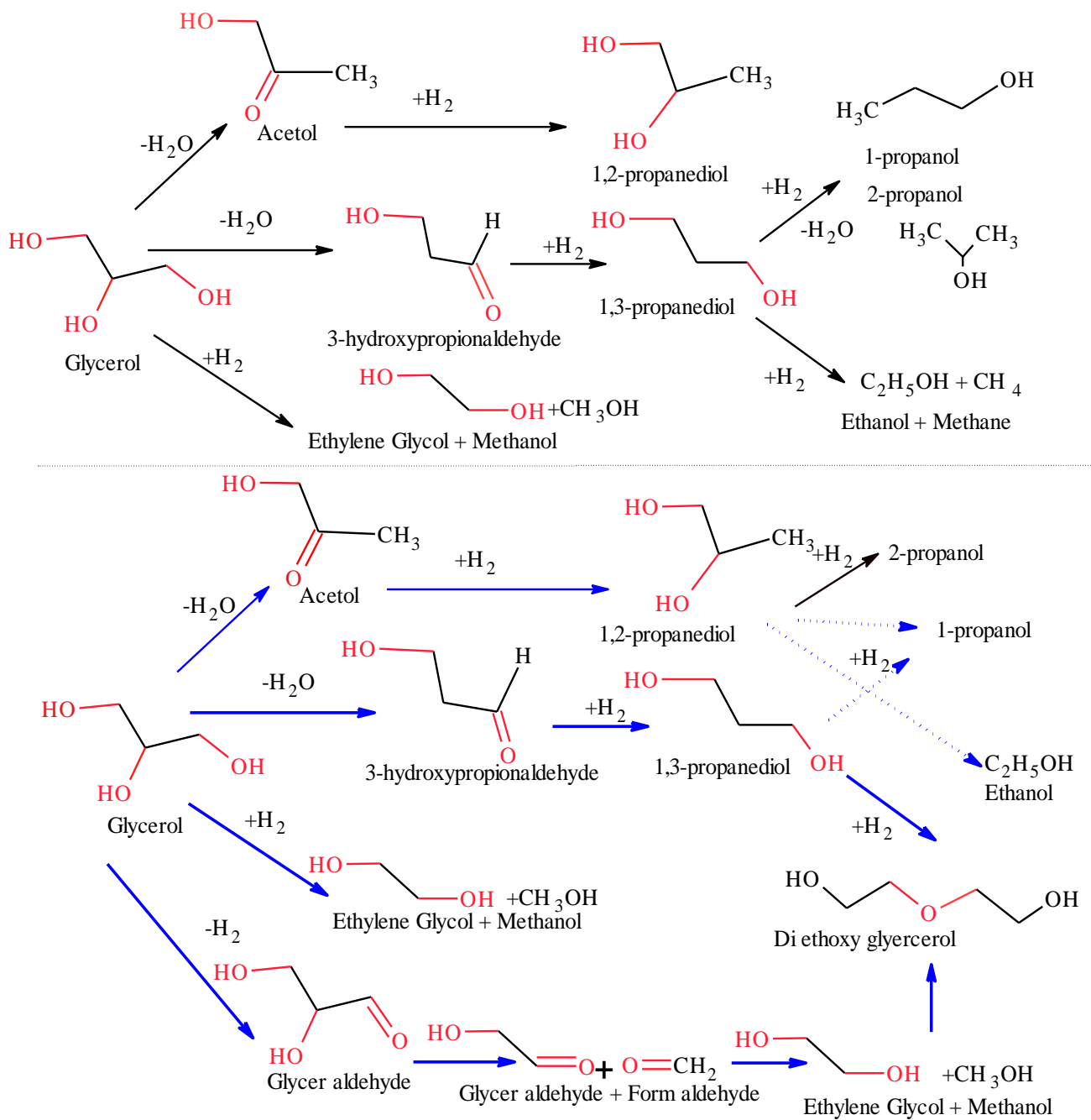


344

345

Fig.4. Proposed reaction pathway to the production of primary products in glycerol steam reforming over Ni based catalyst.

346           Conclusively, very few literatures are available for reforming of acetone for hydrogen or value-added  
347 chemical production. From above discussion it can be concluded that acetone conversion to hydrogen and other  
348 oxygenates mainly depends on metallic state, type of metal doping, acidity of support and reaction temperature.  
349 It can also be concluded that thermodynamic equilibrium for the reduction of acetone mainly depends redox  
350 potential and reaction temperature. Several reports highlighted the metallic interaction and significance of metal  
351 and support interaction for acetone reforming, and it can be concluded that Ni is essential part of catalytic design  
352 for acetone reforming. Whereas, several compositions such as Ni-Mo/Al<sub>2</sub>O<sub>3</sub>, Ni, Co, Mg, different Ni oxides,  
353 mixed oxide, spinel structure, NiZnO/CeO, Mn, Fe, Cu, Zn, Cu, CuPt and Pt have been investigated by different  
354 researcher. Conclusively, each metal behaved differently for reforming of acetone depends on their stability, coke  
355 formation, deactivation and synthesis design. Among all the reported metals Mn, Fe, and Zn were revealed as not  
356 significantly active for reforming of acetone. Whereas, Ni, Co, Pt, Cu were reported as more significant metals  
357 for acetone reforming for hydrogen production. Fig. 5 represented a general chemical reactions (resketched)  
358 occurs during glycerol hydrogenolysis as summarized by (a) Miyazawa et al. and (b) Bildea et al [70,71].



**Fig. 5.** Chemical reactions occurs during glycerol hydrogenolysis as summarized from (a) Miyazawa et al. and (b) Bildea et al. [70,71].

### 2.3. Catalytic Reforming

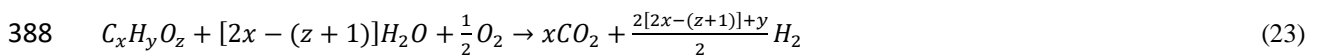
Catalytic reforming in a petroleum refinery is usually operated near the range of 500°C and the reactor's operation pressure is varied according to the high-pressure processes (20-50 bar), medium pressure (10-20 bar) and low-pressure (3-10 bar), depending on the feedstock quality [72]. To date, very few research has been carried out on the selected oxygenated hydrocarbons catalytic reforming, specifically, without steam addition; however,

367 several works were published earlier with reference to glycerol degradation [73], glycerol hydrogenolysis [74,59],  
368 glycerol and bio-oil valorization to bio-fuels [75], as well as aqueous phase reforming, which will be discussed in  
369 section 2.6 It is anticipated that via catalytic reforming of oxygenated hydrocarbons, a large amount of hydrogen  
370 may be produced as its by-products, however, this is highly demanded for hydrodeoxygenation in bio-fuel  
371 refineries [76,77].

## 372 **2.4. Autothermal Reforming**

373 Autothermal reforming, also called oxidative steam reforming, is a combination of a partial oxidation  
374 process, which is a highly exothermic reaction, and steam reforming as an endothermic reaction [78].  
375 Autothermal, emerging from the idea of self-sustained reforming, is an attractive option since it has higher energy  
376 efficiency, improves the system temperature control, reduces the formation of hot spots and avoids catalyst  
377 deactivation by sintering or carbon deposition [78]. Aartun et al. [79] reported that autothermal reforming or  
378 oxidative steam reforming has the main advantage of initial oxidation reaction that is extremely exothermic, in  
379 which it can generate heat for the subsequent endothermic reforming reactions. Thus, this technology has high  
380 potential for saving heating costs that complements the amount of hydrogen produced. However, autothermal  
381 reforming poses difficulty in controlling for a steady-state operation, and, therefore, utilization of the catalyst is  
382 under optimized [80].

383 The efficiency of autothermal reforming is always countered by lower hydrogen yield compared to steam  
384 reforming due to its thermodynamic limitation. Another setback is the cost of the separation process if air is used.  
385 Otherwise, if pure oxygen is used, there is a requirement to set up an additional plant for oxygen generation, hence  
386 incurring very high cost [36]. A general stoichiometric reaction for a complete conversion of an oxygenated  
387 hydrocarbon is as follows:



389 Taking the example of ethanol as one type of oxygenated hydrocarbon undergoing autothermal reforming  
390 process, ethanol is converted to the products, following the combination of partial oxidation of ethanol and steam  
391 reforming of ethanol, as follows:

392 Partial oxidation:



394 Combining with equation 23, autothermal reforming of ethanol (ATRE) is as follows::



396 The autothermal reforming of ethanol is usually operated between 500 – 800°C and it operates at  
397 atmospheric pressure [81]. The feedstock, which consists of the mixture of hydrogen and ethanol, is vaporized  
398 between 180 and 200°C [82]. Prior to feeding the reactants into the reactor, the mixture is injected with oxygen,  
399 which heats up the reactor and thus enables it to reach a higher temperature range.

400 In our recent studies, the thermodynamic analysis of autothermal reforming of oxy alcohols consist of  
401 homologues series of “OH” group such as ethanol, propylene glycol, ethylene glycol and glycerol were  
402 studied[83-86]. The main concern of this study was to compare the effect of thermoneutral condition where no  
403 external air/oxygen supplied for the reaction to sustain and controlled amount of air/oxygen supplied. Our findings  
404 were included that the higher number of oxygen atoms in these homologues’ molecule, the higher tendency of the  
405 reaction to be sustained at the desired temperature, and thus it only requires lesser amount of air for heating. The  
406 hydrogen selectivity however depends on the ratio of hydrogen atoms with respect to the oxygen atoms in each  
407 molecule. The presence of air however, though providing extra heating to the reactor, is offset by a lower hydrogen  
408 production[87].

409 Veiga et al.[69] investigated the production of hydrogen rich gaseous mixture from steam and oxidative  
410 reforming of crude glycerol over Ni (12 wt.%) $-La_2(Ce_{1-x}Zr_x)_2O_7$  (x=0, 0.5, 1). The catalysts were prepared by  
411 polymerized complex method based on the reaction route. The steam reforming was performed at 650°C in fixed  
412 bed reactor with feed 30wt.% glycerol solution. The catalysts with highest basicity (Ni- $La_2(Ce_{0.5}Zr_{0.5})_2O_7$ ) was  
413 proven to be the best catalyst in terms of activity. Oxidative steam reforming was successfully achieved with  
414 highest hydrocarbon yield over all the catalysts. Whereas, the catalyst containing both Ce and Zr showed best  
415 catalytic performance for hydrogen production and low deactivation of the catalyst.

## 416 **2.5. Dry Reforming**

417 Dry reforming, also known as carbon dioxide reforming, is a reforming reaction between oxygenates and  
418 carbon dioxide to produce syn gas, i.e. hydrogen and carbon monoxide. To date, in comparing among all  
419 oxygenates selected; only ethanol has been researched so far in the context of dry reforming [88,89]. Although  
420 research on carbon dioxide reforming of ethanol, known as dry reforming of ethanol (DRE), is not as established  
421 as SRE and ATRE, there is a growing interest in this reforming technology due to cheap reactant costs and a



422 commitment to the reduction of CO<sub>2</sub> in the environment, hence converting the syngas into a valuable product [39].  
423 DRE is a strongly endothermic reaction ( $\Delta H^{\circ}_{298K} = 296.7$  KJ/mol). The stoichiometric reaction of DRE is as  
424 follows:



426 However, the above reaction needs to be carefully controlled since there are many competitive side  
427 reactions taking place, such as dehydrogenation of ethanol to acetaldehyde, dehydration of ethanol to ethylene or  
428 decomposition of ethanol into CO, CO<sub>2</sub> or acetone. Thus, enough CO<sub>2</sub> supply is highly crucial to ensure optimum  
429 H<sub>2</sub> production. DRE may take place between 500 – 1100°C with the optimum range reported to be between 950  
430 – 1050°C. It is important to operate DRE at a high temperature to reduce coke formation, and, ultimately, high H<sub>2</sub>  
431 selectivity [39].

432 In recent studies another experiment was designed by Moretti et al. [90] to study the ethanol steam reforming by  
433 using Nickel and bimetallic Ni-Co supported on ceria zirconia mixture. The investigation revealed that ceria and  
434 zirconia facilitated the metal oxide reduction of metal supported oxide phases. Among all the reported catalysts  
435 formulation Moretti et al. [90] suggested the CZ91NiCo catalysts showed the high ethanol conversion to hydrogen  
436 and selectivity towards CO<sub>2</sub> was found to be more than 500°C [90]. Recently, our studies showed that the 15%  
437 of NiCaO give the highest hydrogen yield and glycerol conversion that peaked at 24.59 % and 30.32% [91].

## 438 **2.6. Partial Oxidation**

439 Partial oxidation is another reforming technology to convert the oxygenated hydrocarbons into hydrogen  
440 and CO<sub>2</sub> or syn gas. In this reforming technology, the reaction is exothermic in nature, where it is not required to  
441 provide external heating other than the supply of air or pure oxygen. Complete oxidation (air supply in excess)  
442 will burn the fuel or reactant completely, hence reducing the amount of hydrogen produced. Therefore, the amount  
443 of air or oxygen supplied may need to be carefully controlled to yield the optimum products. The stoichiometric  
444 equation of partial oxidation is as follows and applies to all oxygenates:



446 In order to obtain syn gas (CO and H<sub>2</sub>), ethanol and propylene glycol would require ½ mol of oxygen  
447 additionally, which is less than what is required for conversion to CO<sub>2</sub> and H<sub>2</sub>. However, ethylene glycol and  
448 glycerol stoichiometrically would not require any additional air to decompose into syn gas as both O/C ratios are

449 1. Partial oxidation studies (thermodynamic study or experimental work) have been carried out extensively on  
450 ethanol [92-94] but very few have been conducted on glycerol [95,96] and recently one on sorbitol [97]. Catalytic  
451 partial oxidation needs to be operated at high temperature and low pressure to inhibit coke formation, and,  
452 ultimately, obtain high hydrogen selectivity [98].

## 453 **2.7. Aqueous Phase Reforming**

454 Aqueous phase reforming [99], also known as hydrothermal reforming, is the reforming in an aqueous  
455 phase. This is a reforming technology that operates in excess water content, at lower temperature (generally  
456 between 200 – 300°C) and high pressure up to 60 bars. APR is highly suitable for oxygenated hydrocarbons,  
457 mainly polyols, due to the presence of oxygen that weakens the C-C bond, and thus allows for easier splitting  
458 between hydrogen and CO. CO could further undergo the water gas shift reaction to be converted to CO<sub>2</sub> [100].  
459 However, for the case of typical hydrocarbons, which only contain C & H atoms, the bonding energy is greater,  
460 hence APR is not an attractive choice. Fig. 6 shows a typical reaction pathway for reforming technology using  
461 various renewables raw materials such as bio-oil, carbohydrates and bioethanol for hydrogen production.

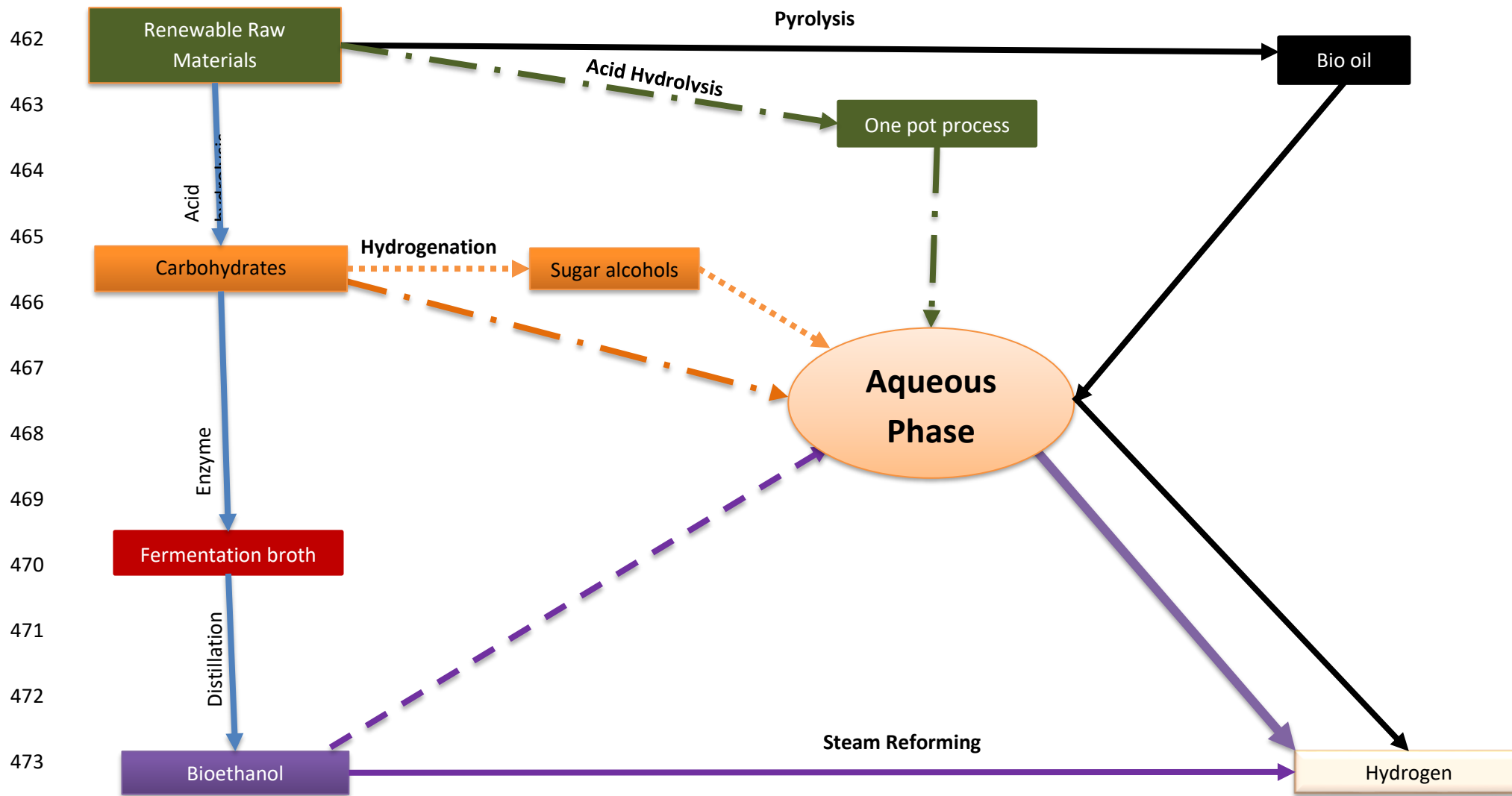


Fig 6. A summary of hydrogen production using reforming technologies.

475 In order to improve the hydrogen production and lower the CO level, in their work, Xu et al. [101] improved the  
476 alkalinity of the process, i.e. by using alkaline-based support for the catalyst. This is supported by Wen et al. [102]  
477 who, by using Pt on alkaline support, yielded a much higher hydrogen molar concentration as well as a higher  
478 hydrogen formation rate. In addition, by using acidic support, the formation of alkanes is increased. APR was also  
479 conducted in glycerol [103] and ethylene glycol [104]. Manfro and colleagues [103] outlined the reaction route  
480 of the process, which involves the breaking of C-C cleavage bonds as well as C-H bonds to form adsorbed species  
481 on the catalyst surface, especially CO (Equation 29). Once CO is adsorbed, it will undergo a water gas shift  
482 reaction, as shown in Equation 30. The reaction scheme is shown as follows:



485 The reaction was carried out by purging He to remove air, in which 250 mL of aqueous solution was  
486 used, consisting of either 1 or 10 wt.% of glycerol. The catalytic test was performed at 250 and 270°C, resulting  
487 in autogenous pressure of 37 and 52 atm. The maximum conversion reached during the catalytic test was 30%,  
488 within 6 reaction hours, with the hydrogen mole fraction on a dry basis being between 70 – 90%. Based on the  
489 test, they suggested that by increasing the weight percentage of glycerol from 1% to 10%, a decrease in glycerol  
490 conversion and hydrogen production was discovered.

491 Similarly, the thermodynamic studies of glycerol was carried out by Seretis et al. [105] via aqueous phase  
492 reforming using the Gibbs free energy minimization method. Seretis et al investigated the effects of different  
493 parameters such as water to glycerol mass ratio (W/G =4-14), temperature (3 - 227°C) and pressure ratio P=P sat  
494  $H_2O \frac{1}{4} 1-2$  for production of hydrogen, methane and carbon. The critical investigation suggested glycerol  
495 conversion reached up to 100% with hydrogen selectivity up to 70% under the broad-spectrum examination  
496 conditions. Under the similar conditions the methane formation was observed to be less at low pressure and high  
497 temperature. Since the reported results showed that methanation was thermodynamically preferred over hydrogen  
498 production. Beside this, it was also observed that glycerol conversion into carbon was found to be up to 80%.  
499 From all the investigation Seretis et al. [105] suggested that carbon can be eliminated at pressure ratio P=P sat  
500  $H_2O \leq 1:4$  and temperature values T N 126.85 °C. The overall conclusion for all investigation suggest that the  
501 optimal W/G for  $H_2$  production was found equal to 9 under thermodynamic equilibrium conditions [105].

502

### 503 3. Catalyst development

504 The catalysts that can be used for other oxygenates are classified into noble metal and non-noble metal (Transition  
505 Metal) catalysts.

#### 506 3.1. Transition metal catalyst

507 A common non-noble metal catalyst that is usually used is nickel, which has been long established for  
508 natural gas reforming, with alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) as its support [106]. However, oxygenates can easily dehydrate and  
509 form ethylene, which can pose serious coking problems by undergoing polymerization that is promoted by the  
510 acid sites of alumina [107]. Ethanol steam reforming via Ni/Al<sub>2</sub>O<sub>3</sub> was also studied by several researchers [108-  
511 110], mainly to investigate any possibility of modification in catalysts formulations .

512 As for glycerol, a Ni-based catalyst has also been widely used in much of the research. Sanchez et al.  
513 [111], Adhikari et al. [112] and Cheng et al. [113] demonstrated steam reforming of glycerol using a Ni-catalyst.  
514 Sanchez et al. and Cheng et al. worked on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Both findings agreed that coke formation is  
515 inevitable with this type of catalyst. Sanchez and colleagues focused on a Ni catalyst with Al<sub>2</sub>O<sub>3</sub> as support and  
516 operating at a very high steam to fuel ratio (16:1) to avoid possible dehydration. Based on the Temperature  
517 Programmed Reduction (TPR) analysis, Ni- in Al<sub>2</sub>O<sub>3</sub> existed within three states: (i) Bulk or free NiO (< 400°C)  
518 [114] NiO bonded to Al<sub>2</sub>O<sub>3</sub> (between 400 and 690°C) and (iii) NiO incorporated into Al<sub>2</sub>O<sub>3</sub>, i.e. formation of  
519 NiAl<sub>2</sub>O<sub>4</sub> (> 700°C). The formation of NiAl<sub>2</sub>O<sub>4</sub> may result in a difficulty to reduce the nickel prior to the reforming  
520 reaction. They further concluded that the catalyst deactivation was associated with the increase in the weight  
521 hourly space velocity (WHSV), i.e. operating at low catalyst loading, hence affecting the hydrogen selectivity.  
522 However, the changes of temperature (within range of 600–700°C), did not significantly affect the hydrogen  
523 selectivity. Nevertheless, a stable catalyst can be achieved for a longer period at a higher operating temperature.

524 Researchers have focused on selectivity of catalysts towards the hydrogen production from various  
525 oxygenates, glycerol is one of them for steam reforming. Similarly, Sad et al. [115] recently investigated Pt based  
526 catalysts for glycerol steam reforming reaction for production of hydrogen. As the steam reforming reaction based  
527 on two steps firstly decomposition of glycerol and secondly water gas shift reaction (WGS). Sad et al. [115] tested  
528 Pt supported by different physiochemical properties catalysts (SiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) for steam reforming  
529 of glycerol (10 wt.% aqueous solution). The reaction carried out at the temperature range of 300-350°C. The  
530 glycerol conversion was found to be 100% with 78.8% hydrogen yield over Pt/SiO<sub>2</sub>. Acidic support like Al<sub>2</sub>O<sub>3</sub>

531 and MgO favored the adverse reaction directing towards the liquid product and coke precursors. Sad et al. [115]  
532 reported the water gas steam reaction at compatible reaction conditions over Pt/SiO<sub>2</sub> and Pt/TiO<sub>2</sub> and Pt/CeO<sub>2</sub> and  
533 Pt/ZrO<sub>2</sub> were found with highest CO conversion at 350°C. They also tested the double bed catalytic system of 0.5  
534 wt. % Pt/SiO<sub>2</sub> and 0.5 wt.% Pt/TiO<sub>2</sub> to study the effect on hydrogen production. It was observed that by using  
535 double bed catalytic system the hydrogen yield increased up to 100% without deactivation on stream [115].

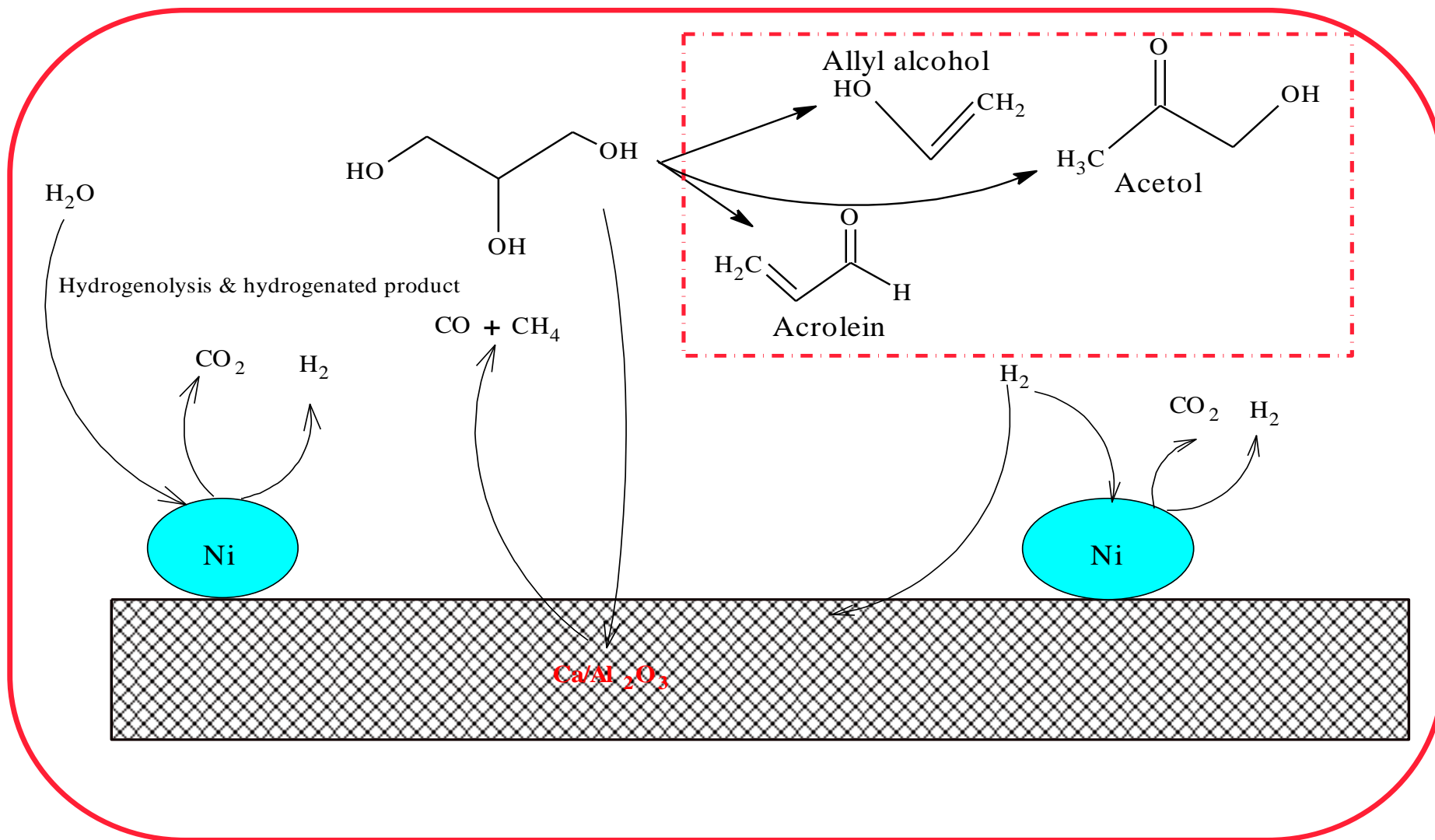
536 Recently, Ochoa et al. [116] has investigated the hydrogen production in two step process, comprising  
537 of pyrolysis and subsequent steam reforming of volatiles produced during pyrolysis. Pyrolysis was performed at  
538 500°C in a conical spouted bed reactor in line with catalytic steam reforming of volatile products of pyrolysis in  
539 fluidized bed reactor at 600°C over Ni supported catalysts. Ochoa et al. [116] reported for satisfactory conversion  
540 above 98% of volatiles with 90% hydrogen yield within first 50 minutes of time on stream. However, catalysts  
541 led to deactivation due to sintering Ni on the catalyst. Ochoa et al. [116] reported that his research team was able  
542 to decrease temperature and other reaction parameters but it ultimately lowered the hydrogen yield.

543 Doukki et al. [117] investigated the glycerol steam reforming over Ni and NiPt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in  
544 aqueous phase reforming for hydrogen production. Doukki et al. [117] actually investigated the hydrothermal  
545 stability of the catalysts that were prepared with different preparation methods i.e. solgel in basic medium and  
546 impregnation on an in-house sol gel  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. After the detail investigation on characterization Doukki et  
547 al. [117] revealed that sol gel impregnation method was found to be crucial in extending the catalyst life due to  
548 adequate distribution of Ni-Pt metallic particles and good thermal stability of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for aqueous phase reforming  
549 process. Whereas, Sol gel basic catalyst exhibited homogenous dispersion of Ni particles but unstable to show  
550 good catalytic behaviour. Among all the formulations of catalysts ASGI (Alumina SolGel Impregnation) the  
551 activity was reported as NiPt/ASGI7 > NiPt/ASGI6 > NiPt/ASGI5 > NiPt/ASGB7). NiPt/ASGI7 showed good  
552 catalytic activity with stability of 56 hours of time on stream with highest glycerol conversion of 79% and gaseous  
553 products of 57% for hydrogen production.

554 In the same way, Dou et al. [118] investigated the effect of H<sub>2</sub>S and HCl impurities in steam reforming  
555 of naphthalene over synthesized Ni and Fe supported over alumina catalysts and commercial catalysts. The  
556 purpose of the study was to investigate the poisoning effect of HCL and H<sub>2</sub>S on catalysts. Steam reforming was  
557 performed over 790, 850 and 900°C over synthesized and commercial catalysts. Dou et al. [118] revealed that  
558 there was no significant effect of Fe addition on steam reforming and water gas shift reaction. The main effect on  
559 catalytic behavior was mainly due to generation of active sites by H<sub>2</sub>S and HCl. He further reported that H<sub>2</sub>S

560 mainly effects the reforming of naphthalene compared to HCl. Similarly, poisoning was also affected by H<sub>2</sub>S not  
561 by HCl. H<sub>2</sub>S chemisorbed on Ni surface catalysts and forms NiS and start to decrease the active sites available for  
562 hydrocarbons in steam reforming. Whereas, poisoning for water gas shift reaction was affected by both H<sub>2</sub>S and  
563 HCl, and activity was completely restored by removal of H<sub>2</sub>S and HCl from gas. Dou et al. [118] further reported  
564 that H<sub>2</sub>S poisoning can be prevented by performing reforming reaction at higher temperature for naphthalene. The  
565 increase of temperature 790°C to 900°C increased the naphthalene conversion from 40% to 100%. Whereas,  
566 poisoning of water gas shift reaction of reforming of naphthalene was significantly influenced by the structure of  
567 the catalyst. Dou et al. [118] findings revealed that strong binding energy between Ni and alumina support  
568 significantly influenced the minimum loss of water gas shift reaction.

569           Recently Arregi et al. [119] investigated the renderability of commercial Ni catalyst used in steam  
570 reforming of volatiles from pyrolysis of biomass for hydrogen production in successive regeneration cycles.  
571 Catalytic activity for steam reforming was not fully enclosed by coke combustion in first cycle mainly due to  
572 deactivation of Ni sintering but the catalyst reached a pseudo-stable state further from fourth cycle, repeating its  
573 behavior in following cycles. The commercial catalyst was reported as highly active and selective for hydrogen  
574 production. The conversion and hydrogen yield at initial time on stream decreased from first to the sixed cycle,  
575 from 99.7-90.1% and from 93.5 to 72.4% respectively. Fig. 7 shows a general representation of active metal sites  
576 of Ni-Ca/ Al<sub>2</sub>O<sub>3</sub> catalyst in GSR reactions.



577

578

**Fig. 7.** Schematic of Ca doped Nickel alumina surface activity from glycerol steam reforming reaction.



### 579 3.2. Noble Metals and Other Catalysts

580 Apart from nickel[120], noble metal catalysts such as Rh[48], Ru[121], Pt[122], Pd[123], and Ir[124]  
581 have also been widely investigated. It was claimed that the Rh catalyst is among the most efficient catalysts for  
582 the reforming process as experimented by Cai et al. [82]. Though, alumina as an excellent support, CeO<sub>2</sub> is another  
583 support that has gained high interest. CeO<sub>2</sub> is claimed to be a better promoter that can lead to higher dispersion of  
584 metal particles and strong interaction between the metal and the support. Improved stability has also been reported  
585 [125]. However, a frequent start-up and shutdown of the system may lead to the  $\gamma$ -CeO<sub>2</sub> deactivation due to the  
586 formation of carbonate on the surface of the catalyst [126]. The use of noble metals has also been reported by  
587 several authors in either ethylene glycol or glycerol reforming technologies, such as Dauenhauer et al. [127] on  
588 autothermal reforming of both components (Rh, Rh-Ce, Rh-La, Pt with ceramic as support), and Chiodo et al.  
589 [48] on the comparison of Rh- with Ni- performance on glycerol steam reforming.

590 Lately, Ramesh et al. [128] further studied the steam reforming of glycerol to hydrogen at low  
591 temperature by using copper decorated perovskite catalysts under the reaction condition of vapor phase. In  
592 comparative studies of all catalysts, LaNi<sub>0.9</sub>Cu<sub>0.1</sub>NiO<sub>3</sub> showed best conversion (73%) of glycerol and selectivity  
593 for (67%) hydrogen. The catalyst characterization was performed before and after the reaction. During the TPRO-  
594 H<sub>2</sub>, it was observed that perovskite structure decomposed to La<sub>2</sub>O<sub>3</sub>, Ni and Cu. The nano particles were generated  
595 by the deposition of Cu on Ni. The decoration of Cu increased the reduction of active Ni species with adequate  
596 basicity. It was observed that the activity of catalysts decreased with increment of Cu concentration.  
597 (LaNi<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>3</sub>) was found to be active till 24 h at 650°C. The researchers observed that TGA analysis showed  
598 that the copper decorated catalysts have enough resistance for coke formation as compared to perovskite catalysts.  
599 It was determined by the authors that the accumulation of copper in perovskite oxide and generation of Cu/Ni  
600 nano particles enabled the dehydrogenation and decomposition of glycerol in steam reforming [128].

601 Li et al. [129] performed the ethanol steam reforming over BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> catalyst over  
602 Ni supported catalysts [129]. The catalyst is reported for 100% conversion into various gaseous products such as  
603 H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> depending on reaction temperature range between 500-750°C. The hydrogen yield of  
604 hydrogen and CO was reported as 85% only for the reaction carried out below 600°C and decrease to 80% at  
605 650°C and 750°C. Li et al. [129] stated that methane amount below 10% at all temperatures. By decreasing  
606 hydrogen to ethanol ratio from 5 to 3 results in several percent increase for CO and decrease for hydrogen and  
607 CO<sub>2</sub>.

608 Huang et al. [130] performed the glycerol steam reforming over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst with addition of Ca-  
609 Mg and La-Ce-Zr oxides as support exhibit the excellent catalytic activity for higher production of syngas. Huang  
610 et al. [130] reported CO<sub>2</sub> <2.8% and methane (0.07%) in syngas produced via glycerol steam reforming. Author  
611 also reported that reforming gas (H<sub>2</sub>-CO<sub>2</sub>)/(CO+CO<sub>2</sub>) molar ratio was determined approximately 2.09. Author  
612 introduced methane in glycerol steam reforming system in order to inhibit the CO<sub>2</sub> production through dry  
613 reforming. The optimized condition for syngas yield was determined as 87.7% on glycerol conversion, that was  
614 much higher than that in glycerol steam reforming without methane.

615 Recently Remiro et al. [131] reported the deactivation mechanism of commercial catalyst Rh/CeO<sub>2</sub>-ZrO<sub>2</sub>  
616 for steam reforming of raw bio-oil. Moreover, regeneration, reusability and reason for deactivation of fresh and  
617 regenerated catalysts was also investigated in detail. Steam reforming was followed by pyrolysis oil in two unit  
618 in series as reactor under suitable temperature. Remiro et al. [131] reported that structural changes were  
619 irreversible and occurred rapidly. The deactivation selectivity affects the reforming of oxygenates from lowest to  
620 highest reactivity. Rh sintering was not significantly cause deactivation at reaction temperature; it was an  
621 unindustrialized deactivation cause at (700°C).

### 622 **3.3. Effect of promoters**

623 Promoters are usually added to the catalyst for modifying the catalytic support structure, and, hence, the electron  
624 distribution property within the catalyst system to enhance its reaction performance. However, using it alone had  
625 no catalytic effect on the reaction. Among the promoters that have been tested since las decade for the purpose of  
626 research in reforming works were: Ca [132], Mg [133,134], Gd [135], Nb[136] , Zr [137], and La [138]. The  
627 research work on group II-doped catalysts on oxygenated hydrocarbons reforming is one of recent interest. Due  
628 to its basicity, doping with calcium and magnesium is hypothesized to be able to reduce the acidity of alumina as  
629 support; hence, inhibiting the dehydration of oxygenates that lead to the formation of ethylene. The research works  
630 associated with promoting calcium to Ni/Al<sub>2</sub>O<sub>3</sub> were carried out by Choong et al. [132], Elias et al. [139] and  
631 Vizcaino et al. [140] on ethanol steam reforming. Vizcaino et al. also studied on Mg addition to Ni/Al<sub>2</sub>O<sub>3</sub> [140].  
632 A comprehensive literature is tabulated in Table 2 based on transition metal and noble metal catalysts for  
633 oxygenates reforming.

634

**Table 2.** The performances of metal-supported and noble metal catalysts in oxygenates reforming.

Feedstock	Catalyst	Temp (°C)	C <sub>2</sub> H <sub>6</sub> O/H <sub>2</sub> O/O <sub>2</sub> (molar ratio)	x C <sub>2</sub> H <sub>6</sub> O (%)	SH <sub>2</sub> (%)	Ref
Bioethanol	Ni/CeO <sub>2</sub> -ZrO <sub>2</sub>		1:9:0.35			[141]
	RhNi/CeO <sub>2</sub> -ZrO <sub>2</sub>	600		91-100	3.5-4.6	
Ethanol	Ce:Zr = 9:1) Nickel, Cobalt,	250-	1:6		80	[90]
	Nickel-Cobalt (CZ91NiCo)	750		90		
Ethanol	(Ni, Cu, Ru, Pt) and	150-	1:1 (for			[142]
and	bimetallic (Pt-Ni, Pt-Cu, Pt-	650	MSR) or 1:3 (for			
Methanol	Ru/ detonation		ESR)			
	nanodiamond (DND)			High	High	
Bioethanol	Ni/La <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> and	150-	43.69 g/L			[143]
	Ni/CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	350		90	63.6	
Ethanol	18 wt% Ni /α-Al <sub>2</sub> O <sub>3</sub> , 25	600				[144]
	wt% Ni/α-Al <sub>2</sub> O <sub>3</sub>			78	17	
Methanol	Cu/Zn/Al/Zr/ porous copper	240-	GHSV 16,252.4			[145]
	fiber sintered felt (PCFSF)	400	ml/g h).	90	high	
Bio-oil	Ni-Co/Al-Mg	650	S/C ¼ 12			[146]
			mol/mol, Liquid			
			flow rate ¼ 0.12		0.101 to	
			mL/min,	high	0.182 g H <sub>2</sub>	
Bio-oil	Ce-Ni/Co/Al <sub>2</sub> O <sub>3</sub>	700	LHSV of 0.23 h <sup>-1</sup>	94.1	83.8	[147]
Methanol	Cu/Zn-Al <sub>2</sub> O <sub>3</sub>	200-	ND			[148]
		350		51.87	75.4	
Acetic acid	Ni/Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub>	450-	WHSV=134h <sup>-1</sup>	100	High	[34]
	Co/Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub>	650				
Bio-oil	Ni/CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	800	S/C=5	100	High	[149]
	Rh-Ni/ CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>		WHSV=21.15h <sup>-1</sup>			
	Ru-Ni/ CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>					

Ethylene	5 wt% Ni/Al <sub>2</sub> O <sub>3</sub>	600	1:9	36	20	[150]
glycol	3.75 wt% Ni-1.25 wt% Pt/Al <sub>2</sub> O <sub>3</sub>			60	44	
	2.5 wt% Ni-2.5 wt% Pt /Al <sub>2</sub> O <sub>3</sub>			50	40	
	1.25 wt% Ni-3.75 wt% Pt /Al <sub>2</sub> O <sub>3</sub>			40	30	
	5 wt% Pt/Al <sub>2</sub> O <sub>3</sub>			30	30	

636 ND: Not determined; C<sub>Feed</sub>: Feed conversion; SH<sub>2</sub>: Hydrogen selectivity

637

638 This is justified from the literature that the catalyst plays an important role in hydrogen production via  
639 steam reforming. Hammoud et al. [148] recently studied the synthesis of copper supported on calcined hydrotalcite  
640 catalysts using the resulting effect of Zn-/Alumina hydrotalcite. The steam reforming reaction was carried out in a  
641 fixed bed reactor under the mild conditions at the temperature of 200-350°C. The physiochemical properties were  
642 identified in result of characterization technique. From the experimental database of Hammoud et al. [148] it was  
643 evaluated that 10%Cu/Zn-Al showed higher activity (75.44%) of hydrogen was produced with 51.87% of  
644 methanol conversion at 250°C. It was confirmed from the experiment that methanol conversion was found to be  
645 strong function of catalysts reducibility and copper concentration. The activity of catalysts like Cu<sub>2</sub>O also depends  
646 on temperature provided [148]. In our recent studies we reported the CO<sub>2</sub> dry reforming of glycerol for syngas  
647 production. The dry reforming was performed using Ag promoted Ni-based catalysts supported on SiO<sub>2</sub>, the  
648 reaction was performed in tubular reactor at 700°C and CO<sub>2</sub>: glycerol ratio of 1, at ambient pressure. The gaseous  
649 products such as H<sub>2</sub>, CO, and CH<sub>4</sub> with H<sub>2</sub>: CO < 1.0 were included in our findings. The detail reaction studies  
650 revealed that Ag<sub>(5)</sub>NiSiO<sub>2</sub> showed outcomes in highest glycerol conversion and hydrogen yield, accounted for  
651 32.6% and 27.4%, respectively [151].

652 Bastan et al. [152] also examined the effect of promoter over a series of Ni nano catalysts supported with  
653 alumina and MgO for aqueous phase reforming of glycerol in order to determine the optimum catalysts for  
654 hydrogen production. Bastan et al. [152] revealed that the APR activity mainly depend on catalysts promotor ratio.  
655 Furthermore, catalytic activity of NiMgO and Ni/ Al<sub>2</sub>O<sub>3</sub> for both were lower than their corresponding mixed  
656 oxides and catalytic activity increased with Al/Mg ratio. Bastan et al. [152] reported conversion of glycerol (92%)  
657 and hydrogen selectivity (76%).

658 Aqueous phase reforming of crude glycerol was conducted by Larimi et al. [83]. Over 5wt.% PtM/Al<sub>2</sub>O<sub>3</sub>  
659 i.e. (M ¼ Pd, Rh, Re, Ru, Ir, Cr) catalysts for hydrogen production. Larimi et al. [83] reported that the catalytic  
660 performance mainly depend on both active metal loading and type of promoters. Among all the formulations 5  
661 wt.% Pt loading with Rh/ Al<sub>2</sub>O<sub>3</sub> was observed to be the best for the catalytic activity for hydrogen production rate  
662 42625 mmol/gcat h<sup>-1</sup>) and selectivity of (89%) in APR of 10wt.% pure glycerol solution.

663 Phongprueksathat et al. [34] performed the catalytic steam reforming of acetic acid over Ni, Co supported  
664 by Ce-Zr oxide at reaction temperature of 450-650°C. The author reported that Ni/CeZrO<sub>2</sub> and CoCeZrO were  
665 found to be potential catalysts to activate the Ce-C bond cleavage and reforming of cracked intermediates. He  
666 found Ce-ZeO<sub>2</sub> (CZO as an active support in steam reforming of acetic acid that favours the ketonization reaction  
667 rather than C-C bond cleavage reaction at lower temperature. He reported that Ni/CZO catalyst was more active  
668 for acetic acid steam reforming due to higher Ce-C bond cleavage activity than Co-CZO catalysts.

### 669 **3.4. Catalysts preparation methods**

670 The effectiveness of the reforming process is also influenced by the catalyst preparation method. The  
671 most common catalyst preparation method demonstrated by most of the researchers are wet impregnation,  
672 incipient wetness impregnation and co-precipitation methods. Each method of catalysts preparation gives different  
673 effect on the physicochemical properties of the catalysts such as surface area, metal-support interaction, binding  
674 energy, particle shapes and sizes, and the dispersion of metal particle over the surface of the catalyst. The choice  
675 of catalyst preparation method helps in reducing the agglomeration of the particles which usually cause sharp  
676 deactivation of the catalysts[153].

677 Neto et al. [154] studied on the effect of preparing Ni based catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> using three  
678 different methods which are nanocasting (NiAlN) , co-precipitation(NiAlC) and incipient wetness  
679 impregnation(NiAlW) for glycerol dehydration reaction. It was found that different catalyst preparation method  
680 possesses different physicochemical properties of the catalysts. NiAlN exist in mesoporous structure with the  
681 highest specific area and pore size compared followed by NiAlW and NiAlC which both exist in micropores  
682 structure. The XRD results obtained shows that NiAlC has the highest peak of cubic phase which indicate high  
683 crystallinity of the catalyst compared to NiAlN and NiAlC catalysts. The performance of the catalysts evaluated  
684 for dehydration of glycerol shown that NiAlW had the highest catalytic performance with 19.7% glycerol  
685 conversion and no catalysts deactivation during the reaction. However, the performances of NiAlN and NiAlC

686 decreased with glycerol conversion of only 3.3% and 8% respectively due catalyst deactivation. Table 3 presents  
 687 various methods of catalysts preparation implemented in reforming technologies. There is still a huge gap to be  
 688 focused on catalysts preparation method and study the physicochemical properties on various applications.

689 **Table 3.** Catalysts preparation method for reforming process.

Catalyst	Preparation method		Reforming technique	Feed	Operating condition			Results		Ref
					Temp (°C)	Pressure (atm)	Feed conc (wt%)	C <sub>Feed</sub> (%)	SH <sub>2</sub> (%)	
Ru/γ-Al <sub>2</sub> O <sub>3</sub>	Wet	co-	Steam	Glycerol	400-	1	20	35-	High	[155]
	impregnation		reforming		800			92		
Ru/B <sub>2</sub> O <sub>3</sub> -	Wet	co-	Steam	Glycerol	400-	1	20	15-	High	[155]
Al <sub>2</sub> O <sub>3</sub>	impregnation		reforming		800			85		
Ru/MgO-	Wet	co-	Steam	Glycerol	400-	1	20	20-	High	[155]
Al <sub>2</sub> O <sub>3</sub>	impregnation		reforming		800			55		
2 wt%	Sol-gel		Steam	Glycerol	400-	1	10	10-	42-	[156]
Mo/Al			reforming		500			40	55	
5 wt%	Sol-gel		Steam	Glycerol	400-	1	10	15-	40-	[156]
Mo/Al			reforming		500			40	50	
12 wt%	Sol-gel		Steam	Glycerol	400-	1	10	18-	35-	[156]
Mo/Al			reforming		500			50	45	
10 wt% Ni/	Co-		Aqueous	Glycerol	250	25	10	62	85	[120]
CeO <sub>2</sub>	precipitation		phase							
			reforming							
10 wt% Ni/	Co-		Aqueous	Glycerol	250	25	10	87	66	[120]
Ce <sub>0.7</sub> Zr <sub>0.3</sub> O <sub>2</sub>	precipitation		phase							
			reforming							
10 wt% Ni/	Co-		Aqueous	Glycerol	250	25	10	55	79	[120]
ZrO <sub>2</sub>	precipitation		phase							
			reforming							

		Aqueous	Glycerol	240	40	10	84	86	[157]
12Ni-	Sonochemical	phase							
1Cu/MWNT	method	reforming							
Pt	Incipient	Aqueous	Glycerol	225	29.3	10	ND	31	[158]
(2.77wt%)/	wetness	phase							
Al <sub>2</sub> O <sub>3</sub>	impregnation	reforming							
		Aqueous	Glycerol	250	50	10	92	76	[152]
Ni/Al <sub>2</sub> Mg	Co-	phase							
	precipitation	reforming							
Pt/Al <sub>2</sub> O <sub>3</sub>	Incipient	Aqueous	Glycerol	225	29	10	ND	17	[159]
	wetness	phase							
	impregnation	reforming							

---

690 ND: Not determined; C<sub>Feed</sub>: Feed conversion; SH<sub>2</sub>: Hydrogen selectivity

691

#### 692 4. Merits and Demerits

693 The renewable and sustainable energy system has been developed in the last few decades. To develop  
694 the most promising clean system, energy produced from hydrogen has been targeted for an interest of many  
695 researchers. Hydrogen produced from glycerol and ethanol steam reforming are the most common among them.  
696 Glycerol is by-product of many industrial processes such as methyl and ethyl esters, soap and biodiesel production.  
697 The GSR process has been developed for hydrogen production on lab-scale because it does not need any further  
698 changes in industrial process based on steam reforming. The selection of catalysts for hydrogen production via  
699 GSR process is an important and fundamental need. Catalysts have been developed using various noble metal for  
700 hydrogen production in GSR process such as Rh, Ru, Pt, Pd and Ir. Although these expensive catalysts give good  
701 yield of hydrogen, but researcher are always interested in finding cheaper and highly active catalysts. Based on  
702 these results Ni based catalysts become significant in hydrogen production for many researchers. The Ni based  
703 catalysts are quite cheaper, highly active, and more stable and allow working at lower temperature. Nevertheless,  
704 in the last few decades great efforts have been put on for Ni-based catalysts with development of various promoters  
705 to enhance the catalytic performance. For any catalytic activity and efficiency, support must play an important  
706 role. The influence of support must be considered during the development of catalysts. The support as neutral  
707 shows higher thermal stability and lower coke formation. The proper promoter used and wt.% doped on support

708 also necessary in order to enhance the catalytic activity and stability. This is still an interesting field to work for.  
709 Subsequently, further research needs to be done for this area, to ensure that the catalyst is active at lower  
710 temperature and stable for longer time utilization, without significant coking issues.

711 Various mechanisms have been proposed for GSR and ESR reactions. The most common is Langmuir–  
712 Hinshelwood dual site mechanism with adsorption phenomenon. Nonetheless, a detail study has not been done  
713 yet for this process, and thus further research is required to deal with its mechanism. Furthermore, since the GSR  
714 reaction prone to high carbon deposition, the detailed studies for coke formation with its kinetics has been done  
715 but more investigation is required. However, more focus is required to study how these cokes may form on the  
716 catalyst surface and how to reduce the production of it, or catalyst regeneration that allow the coke to be removed.  
717 The good catalysts together with more suitable operating conditions have been widely studied for GSR and ESR,  
718 but the thermodynamic limitations for glycerol and ethanol conversion and hydrogen yield are still part of  
719 discussions for many researchers.

720 In order to deal with intensified process of GSR, the separation of CO<sub>2</sub> from H<sub>2</sub> within the same pot  
721 continuously while reacting can be a great deal. It has been found that the removal of CO<sub>2</sub> or H<sub>2</sub> from the reaction  
722 mixture, moves the thermodynamic equilibrium towards higher glycerol conversion and high H<sub>2</sub> yields, which  
723 obey the Le Chatelier's principle. However, other operating conditions such as temperature, WGFR, WHSV and  
724 pressure must be dealt carefully to achieve optimum outcome. The CO<sub>2</sub> emissions can easily be evaded through  
725 SEGSR, However, the new solutions combining with catalytic GSR within situ CO<sub>2</sub> and H<sub>2</sub> removal would be an  
726 interesting phenomenon that needs to be researched.

## 727 **5. Conclusion**

728 As per our understanding and analysis from literature, several conclusions could be drawn. Hydrogen  
729 can be produced via various technologies such as steam reforming, autothermal reforming, partial oxidation, dry  
730 reforming, and aqueous phase reforming. These reforming processes for hydrogen production using oxygenated  
731 hydrocarbons production are highly feasible and economical friendly. However, these processes are susceptible  
732 to other side reactions, such as decomposition, dehydration and dehydrogenation that lead to the formation of coke  
733 and hence deactivate the catalyst. Therefore, the choices of catalysts and catalyst preparation method are important  
734 in ensuring high hydrogen selectivity, apart from the manipulation of thermodynamic properties, such as steam to  
735 fuel ratio (steam reforming and APR), temperature and oxygen to carbon ratio (in autothermal reforming).



736 Addition of promoters on the metal based catalyst enhanced the catalyst activity in reforming by either inhibiting  
737 the carbon formation or enhancing the reaction for higher hydrogen yield. These parameters are important to  
738 reduce the side products that would lead to coke formation, hence deactivating the catalyst.

739 Based on this literature study, it is found that the oxygenated hydrocarbons steam reforming is feasible  
740 as demonstrated by many researchers. However, with relation to the series of polyols homologues chosen, only  
741 propylene glycol reforming research has not been reported elsewhere, while researches are intensely focused on  
742 ethanol and glycerol reforming. Nickel is a common catalyst, with many modifications carried out to improve its  
743 performance by either using a different support other than alumina or introducing a promoter to enhance the outlet  
744 gas selectivity. The research on calcium doping to nickel/alumina had only been investigated to date on ethanol  
745 steam reforming, but not yet on other homologues, such as ethylene glycol, propylene glycol and glycerol. While  
746 it was reported that encapsulating carbon and graphitic carbon might form on a typical nickel/alumina catalyst  
747 surface, the presence of calcium as a promoter to this nickel/alumina catalyst is yet to be investigated.

748 While it is found that these technologies are heavily researched in the lab scale, pilot scale research works  
749 are yet to be reported. It is believed that more extensive pilot scale research works need to be carried out within  
750 these few years so the blue hydrogen from the oxygenated steam reforming process can be realized within this  
751 decade. Due to COVID-19, this is the right time to start it right for a greener technology. While the solution is  
752 nearly there, an accelerated study needs to be conducted before the 'old norm' i.e. the fossil fuels claimed their  
753 place again.

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760

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