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

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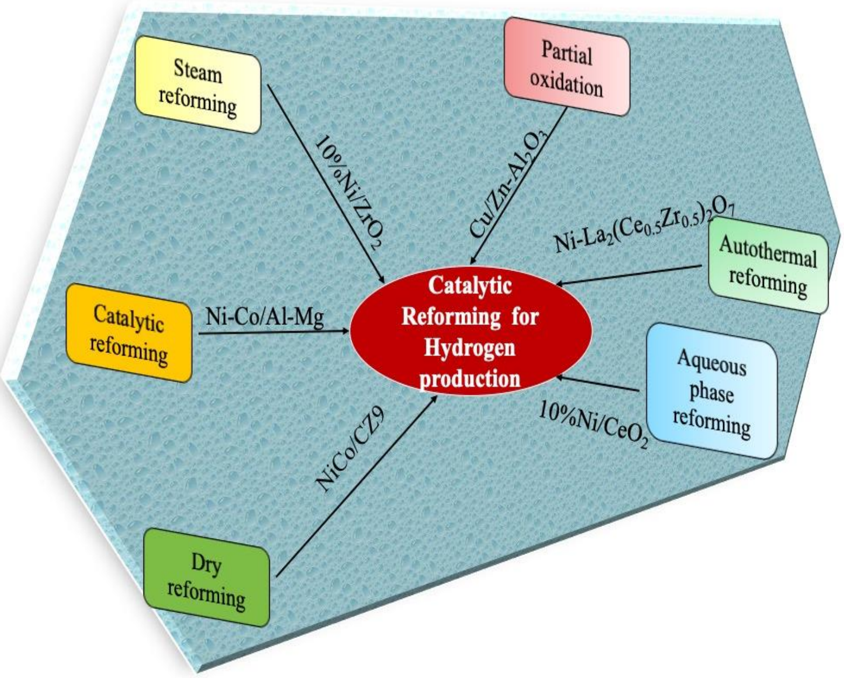
Graphical Abstract



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Abstract

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

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

1. Introduction

The pursuit for a greener environment and struggle to reduce the dependency on fossil fuels has driven mankind to devise better energy solutions. Some of the effective solutions to combat the problem of fossil fuel dependency are the introduction of renewable energy, such as solar energy, wind power and biomass. Extensive research has proven that renewable energy not only extends the shelf life of the exhausting non-renewable fossil fuel but also reduces the level of carbon dioxide in the earth's atmosphere. In the year 2020 while more than 2/3 of the world population are fighting with COVID-19, there are some good news with regards to the CO_2 emission from the industry. It is expected that there will be a drop in CO_2 emission from 4 to 11 % in 2020 [1], but this drop would not be sustainable. Over the next few years, if the governments do not take serious action now, it may overshoot as the trade and industries are trying to fulfil the previous demand or trying to justify continuing any cancelled CO_2-released projects in the past with the reason of relieving the economy. It is also important to provide green stimulus to the renewable energy companies to provide better technology that safeguarding our environment further, without further damaging the economy.

Nevertheless, the problems related to renewable energy sources, however, are still persistent. The sources are generally located at some specific locations. Although they are readily available, these sources are intermittent, such as solar and wind energy, and therefore unstable[2]. The International Energy Agency (IEA) predicts an increasing share of primary energy used from renewables in the future due to support from the government, the falling costs of renewable energy, change in the price of CO_2 emissions in certain regions and the rising price of fossil fuels in the long-term. Due to COVID-19 itself that is considered a blessing in disguise to the world environment, the only right thing needed by the governments is to ensure that CO_2 and other harmful gases released by the fossil fuels to continue decrease, and therefore their responsibility is to stick by the earlier plan to ensure the renewables will be continued to be supported despite a shortfall of the fossil fuel prices.

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

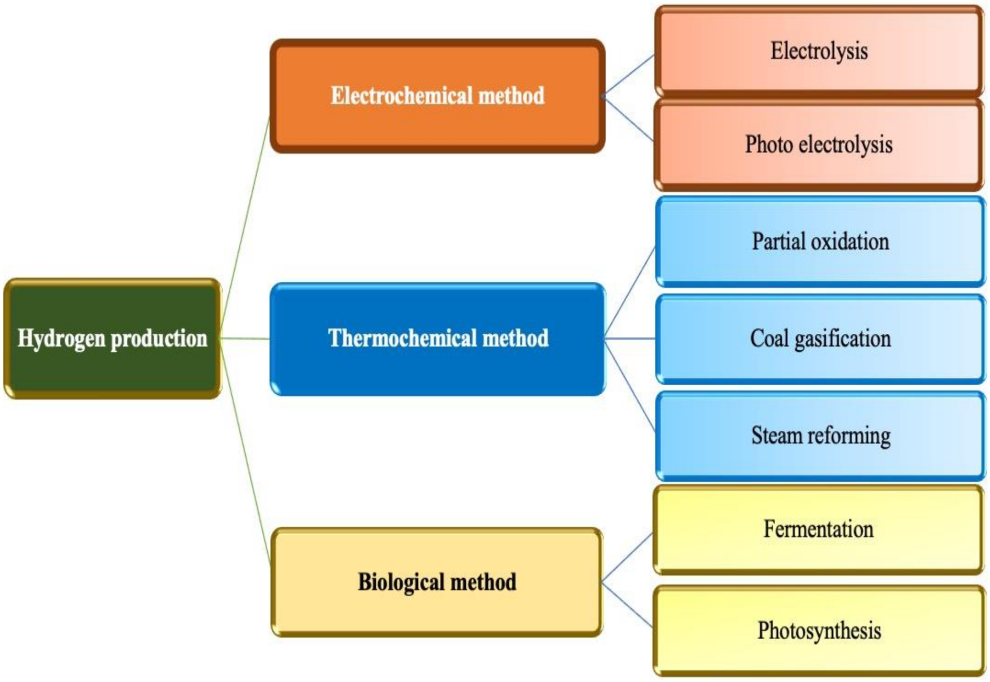


Fig. 1. Hydrogen production using various methods.

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].

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

Presently, hydrogen is mainly produced from industrial natural gas, which is mainly responsible for CO_2 emission known as “grey hydrogen”. Another cleaner version of hydrogen is “blue hydrogen”, of which the hydrogen is generated from carbon emission captured, stored and reused. Among all cleaner hydrogen, “green hydrogen” is the cleanest form of hydrogen produced from renewable sources without emitting CO_2. Currently, grey hydrogen is inexpensive than other two types. However, the increase of the carbon footprint cannot be ignored and to be accepted as a norm. In contrast, the price of blue hydrogen is mainly depending on natural gas price besides the carbon capture store and reuse cost. In present scenario, blue hydrogen is pricier than grey hydrogen in Europe, but it is expected that the price will reduce if the price of CO_2 emission increases in the future. Furthermore, when the process of carbon capture is used, and storage process is scaled up, the blue hydrogen will be cheaper.

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

Reforming is a well-developed thermal technology in which the desired product is mainly hydrogen (H_2) with carbon dioxide (CO_2), carbon monoxide (CO) and methane (CH_4) being the usual side products. This could be considered as the ‘blue’ hydrogen technology as the reforming process is still releasing the CO_2, but it is a derivative from the plants and biomass, and hence the CO_2 released shall revolve in its own cycle. The reformer’s effluents can be varied either thermodynamically or by using different types of catalysts to obtain a high yield of H_2 or syngas. To date, many reforming processes utilizing oxygenated hydrocarbons have been researched. Several reviews has been reported on various technologies [11,12]. These include dry gas reforming, also known as CO_2 reforming, steam reforming, hydrothermal reforming (also known as aqueous phase reforming), partial oxidation and autothermal reforming [13-15]. Among the growing interests of oxygenated hydrocarbons undergoing reforming technologies are the short chain alcohols (monohydric alcohols), such as methanol and ethanol (or bio-ethanol) [16], and polyhydric alcohols, such as glycerol [17,18]. The biomass oil (bio-oil), which is obtained via pyrolysis activity, may also be used to undergo the reforming process, however, the bio-oil consists of a more complex mixture that may include aldehydes, ketones and carboxylic acids [19-21]. Most of these mentioned oxygenates can be obtained from biomass derivative products [22,23]. Glycerol ($C_3H_8O_3$), as an example, is a by-product of biodiesel production [23,24]. Glycerol is widely used in many applications including personal care, food, oral care, tobacco, polymer and pharmaceutical applications. However, the crude glycerol that is obtained from biodiesel production has to undergo an energy intensive distillation process to purify glycerol to an acceptable purity, which is costly [23]. Avasthi et al. [24] reported that, at the moment, biodiesel production is costlier than the petroleum diesel, and that one of the ways to reduce the cost is to utilize the by-product (glycerol) effectively, which is further supported by Quispe et al. [25].

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

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

2. Reforming Technologies

Reforming is a well-developed technology for converting hydrocarbon into molecular hydrogen, and carbon dioxide or syngas (hydrogen and carbon monoxide) at a high temperature of usually between 400 to 800^{o}C. Generally, several main reactions occur during the reforming process. However, it is vital to be aware that reforming technology is highly dependent on the type of reactant used during the process. Hydrogen (H_2) and carbon dioxide (CO_2) are normally released as the main products of a full reactant conversion. However, there are times that carbon monoxide (CO) and methane (CH_4) may also be produced during the process. To date, considerable reforming research and developments have been implemented. These include steam reforming, dry gas reforming, also known as CO_2 reforming, hydrothermal reforming (also known as aqueous phase reforming), partial oxidation and autothermal reforming. Fig. 2 illustrates the overview of reforming technologies and catalyst development, focused in this review.

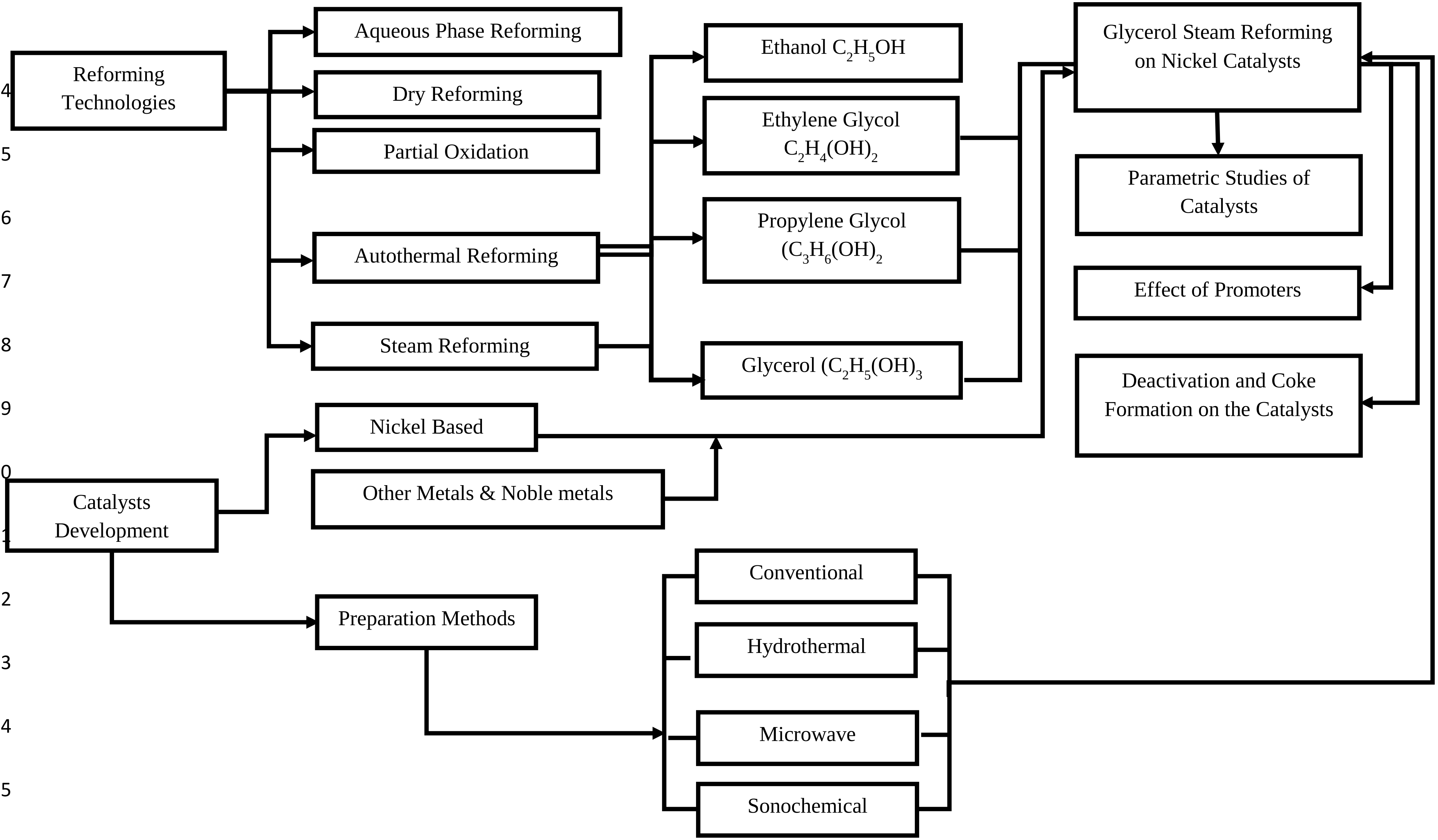


Fig. 2. The overview of reforming technologies, catalysts and its applications.

2.1. Oxygenates for Reforming Technologies

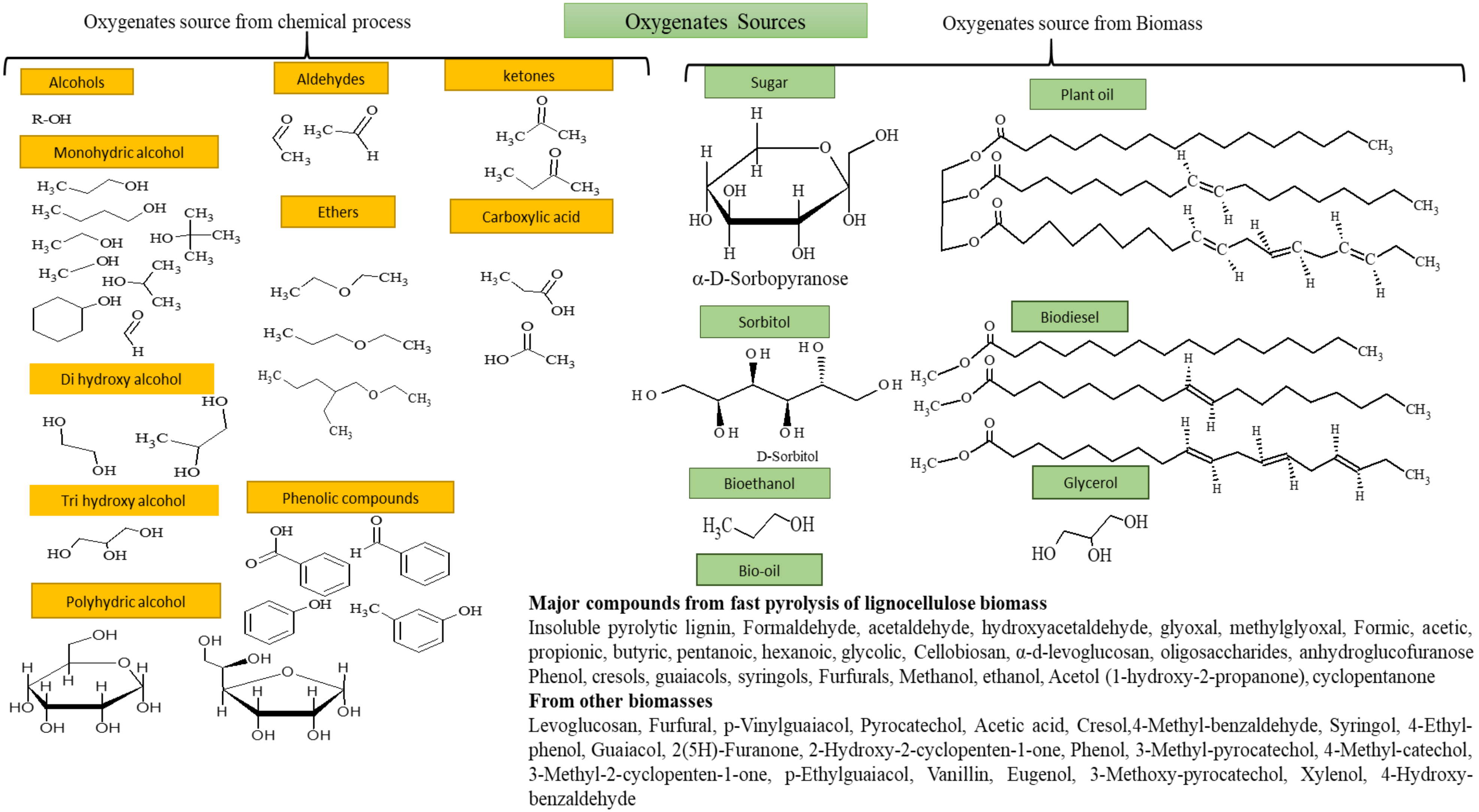
Oxygenated hydrocarbons are considered to be one of the potential sources of fuel for the reforming technology to complement the utilization of natural gas (methane) [26]. The growing interest in oxygenated hydrocarbons includes the short chain alcohols (monohydric alcohols), such as methanol and ethanol (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.

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

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



Major compounds from fast pyrolysis of lignocellulose biomass

Insoluble pyrolytic lignin, Formaldehyde, acetaldehyde, hydroxyacetaldehyde, glyoxal, methylglyoxal, Formic, acetic, propionic, butyric, pentanoic, hexanoic, glycolic, Cellobiosan, α-d-levoglucosan, oligosaccharides, anhydroglucofuranose Phenol, cresols, guaiacols, syringols, Furfurals, Methanol, ethanol, Acetol (1-hydroxy-2-propanone), cyclopentanone

From other biomasses

Levoglucosan, Furfural, p-Vinylguaiacol, Pyrocatechol, Acetic acid, Cresol,4-Methyl-benzaldehyde, Syringol, 4-Ethyl-phenol, Guaiacol, 2(5H)-Furanone, 2-Hydroxy-2-cyclopenten-1-one, Phenol, 3-Methyl-pyrocatechol, 4-Methyl-catechol, 3-Methyl-2-cyclopenten-1-one, p-Ethylguaiacol, Vanillin, Eugenol, 3-Methoxy-pyrocatechol, Xylenol, 4-Hydroxy-benzaldehyde

Fig.3. Commonly used oxygenates for reforming technologies reported in literatures.

2.2. Steam Reforming

Steam reforming is the most common and deep-rooted reforming technology and is well developed in the petrochemical industry to convert natural gas (mainly methane) into hydrogen. This reaction is endothermic in nature. Many research works have focused on improving the performance of this technology using other hydrocarbons, e.g. oxygenated hydrocarbons (e.g. methanol, ethanol, glycerol, dimethyl ether, acetone and acetic acid) or heavier hydrocarbons (C_3 – C_{10} components).

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

$$C_xH_yO_z + (2x - z)H_2O \rightarrow xCO_2 + \frac{2(2x-z)+y}{2}H_2 \qquad (1)$$

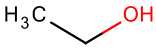
In a complete conversion of an oxygenated hydrocarbon, the reforming reaction is normally accompanied by a water gas shift reaction, as follows:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (\Delta H^o_{298K} = -41.2 \text{ kJ/mol}) \qquad (2)$$

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

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

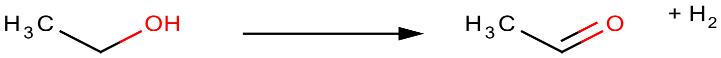
Taking ethanol as an example of oxygenated hydrocarbons for steam reforming reaction will generally follow this stoichiometric reaction:



$$+3H_2O \rightarrow 6H_2 + 2CO_2 \qquad (\varDelta H^{o}_{298K} = 174\text{kJ/mol}) \qquad (3)$$

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

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \qquad (\varDelta H^{o}_{298K} = 68.9 \text{ kJ/mol}) \qquad (4)$$



Acetaldehyde undergoes decomposition to methane and carbon monoxide, respectively:

$$CH_3CHO \rightarrow CH_4 + CO \qquad (\varDelta H^{o}_{298K} = -19.2 \text{ kJ/mol}) \qquad (5)$$

Otherwise, acetaldehyde may undergo steam reforming, as follows:

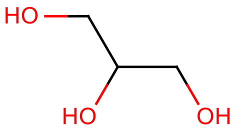
$$CH_3CHO + H_2O \rightarrow 3H_2 + 2CO \qquad (\varDelta H^{o}_{298K} = 296.5 \text{ kJ/mol}) \qquad (6)$$

If reaction (5) has high methane selectivity, eventually, CH_4 will undergo steam reforming to produce hydrogen with CO_2 and/or CO, as shown in equations 7 and 8. CO will further undergo water gas shift reaction (WGS) to produce CO_2 and H_2, as shown earlier in equation (2).

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad (\varDelta H^{o}_{298K} = 165 \text{ kJ/mol}) \qquad (7)$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (\varDelta H^{o}_{298K} = 206 \text{ kJ/mol}) \qquad (8)$$

The temperature range for operating ethanol steam reforming is quite wide, ranging from 300 – 650°C [40-42,38]. With the presence of a catalyst, it is possible to achieve complete conversion of ethanol at 350°C and at atmospheric pressure, whilst a non-catalytic reaction may require a higher temperature for a complete conversion [42]. Glycerol steam reforming research work has been reported by many researchers [43-46] in last decades. Glycerol steam reforming follows this stoichiometric reaction:

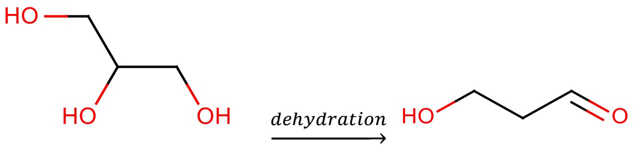


$$+3H_2O \rightarrow 3CO_2 + 7H_2 \qquad (\Delta H^o_{298K} = 128\ \text{kJ/mol}) \qquad (9)$$

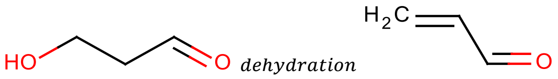
There are a few possible routes of reactions, depending on the type of catalyst and conditions provided to the system, e.g. enough steam to fuel ratio as well as operating temperature. However, most of the research works reported that glycerol decomposed into acetaldehyde, propanal, acetone, acrolein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

$$C_3H_8O_3 \rightarrow 4H_2 + 3CO \qquad (\Delta H^o_{298K} = 251\ \text{kJ/mol}) \qquad (10)$$

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



$$+ H_2O \qquad (\Delta H^o_{298K} = 450\ \text{kJ/mol}) \qquad (11)$$



$$+ H_2O \quad (\Delta H^o_{298K} = -36\ \text{kJ/mol}) \qquad (12)$$

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

$$C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2 \qquad +128\ \text{kJ/mol} \qquad (13)$$

$$C_3H_8O_3 \rightarrow 4H_2 + 3CO \qquad +251\ \text{kJ/mol} \qquad (14)$$

$$C + H_2O \leftrightarrow CO + H_2 \qquad +131\ \text{kJ/mol} \qquad (15)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad -41\ \text{kJ/mol} \qquad (16)$$

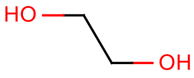
$$C + 2H_2 \leftrightarrow CH_4 \qquad +75\ \text{kJ/mol} \qquad (17)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad -206\ \text{kJ/mol} \qquad (18)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad -165\ \text{kJ/mol} \qquad (19)$$

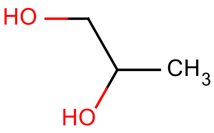
$$C + CO_2 \leftrightarrow 2CO \qquad +172\ \text{kJ/mol} \qquad (20)$$

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



$$+ 2H_2O \rightarrow 2CO_2 + 5H_2 \qquad (\Delta H^o_{298K} = 85.9\ \text{kJ/mol}) \qquad (21)$$

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



$$+ 4H_2O \rightarrow 3CO_2 + 8H_2 \qquad (22)$$

The maximum hydrogen molecular yield possible to be achieved in propylene glycol steam reforming is 2.67 mol/mol C, which is higher than ethylene glycol (Y_{H2} = 2.5) and glycerol (Y_{H2} = 2.33), but relatively lower than ethanol (Y_{H2} = 3). Propylene glycol however has been researched to be produced by glycerol, via hydrogenolysis [59]. All four oxygenated hydrocarbons chosen to make up a series of homologues, which form an interesting set for investigation.

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

Very few studies have been reported for steam reforming of acetone i.e. one of the major by-products of bio-oil. This might be due to very low boiling point and high vapor pressure. Recently, the study was performed by Elias et al. [60] investigated the Ni/ZnO/CeO_2 based catalysts for the steam reforming of acetone for the production of hydrogen. The study revealed that Ni/ZnO with in cooperation of CeO_2 performed better than barely Ni/ZnO. Elias et al. [60] particularly investigated in detail the carbon deposition and catalytic behavior. Ni/xCeZnO firstly produced low coke deposition compared to Ni/ZnO. Secondly, the increase of CeO_2 loading significantly increased the hydrogen production and changed the carbon nature from hard carbon to carbonaceous graphite.

Some other catalysts such as Mn, Fe, Ni, Co, Cu and Zn were investigated for aqueous phase reforming of acetic acid and acetone by Li et al. [61] recently. Based on Li et al. screening of different metal catalysts, it was reported that Mn, Fe and Zn based catalysts were not significantly active for steam reforming of acetone. This result mainly due to low capacity of metals to break the C-O bond. According to Li et al. [61] findings, Co and Cu based catalysts were found to be more active only for methanol steam reforming rather than acetone. The main difference of catalytic activity of Co and Ni was also insignificant. Nonetheless, the reforming of acetone was comparatively more difficult than that of acetic acid due to large molecular size. The difference of catalytic behavior and physicochemical properties of transition metal catalysts should be considered carefully to use in steam reforming of other organic compounds such as acetone, acetic acid and methanol.

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

Suitable vaporization temperature prior to entering the main reactor must also be carefully selected, as high vaporization temperature would favor the glycerol to be decomposed first into other homogeneous reaction products such as ally alcohol, acetol and acrolein[62].In addition to this, different type of promoters and supports would favor either hydrogenolysis, dehydrogenation, condensation, polymerization, hydrogenation or dehydration reactions, which can be explained from Fig. 4, using example of Ni-Ca/Al_20_3 catalyst. As such, GSR is a delicate process, for which the kinetics need to be investigated with care prior to any pilot studies or commercialization purposes. On top of these, the crude glycerol from the biodiesel production may contain a lot more impurities with inconsistent compositions and hence making the technology is much more challenging.

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

Catalyst	Operating Conditions				GSR Conversion %	H Yield (%)	Ref
	T (°C)	P (atm)	FFR (mL min^{-1})	WGFR (h) wt. % glycerol			
10 wt% Ni/ZrO$_2$	650	1	0.06	10	72	65	[63]
10 wt% Ni/SiC	400	1	WHSV=33.3 h^{-1}	9	95.2	NA	[64]
10 wt% Ni/Al	500	1	GHSV=0.95 min^{-1}	W: G=3.5:1 W: G=6:1	25 62	1.2 2.6	[65]
10 wt% Ni/Al	600	1	GHSV=0.95 min^{-1}	W: G=3.5:1 W: G=6:1	56 84	2.2 3.6	[65]
10 wt% Ni-3 wt% Mg/Al	500	1	GHSV=0.95 min^{-1}	W: G=3.5:1 W: G=6:1	40 70	1.8 2.9	[65]
10 wt%Ni-3 wt% Mg/Al	600	1	GHSV=0.95 min^{-1}	W: G=3.5:1 W: G=6:1	61 92	2.5 4	[65]
10 wt% Ni-5 wt% Mg/Al	500	1	GHSV=0.95 min^{-1}	W: G=3.5:1 W: G=6:1	32 64	1.4 2.5	[65]
10 wt% Ni-5 wt% Mg/Al	600	1	GHSV=0.95 min^{-1}	W: G=3.5:1 W: G=6:1	56 82	2.2 3.8	[65]
10 wt% Ni-10 wt% Mg/Al	500	1	GHSV=0.95 min^{-1}	W: G=3.5:1 W: G=6:1	26 30	1.2 1.4	[65]
10 wt% Ni-10 wt% Mg/Al	600	1	GHSV=0.95 min^{-1}	W: G=3.5:1	44 78	2 3.4	[65]

				W: G=6:1			
Ni/γ-Al_2O_3	400-600	1	W/F=1.05 mg min ml^{-1}	20	42-90	22-80	[66]
Ni/B_2O_3-Al_2O_3	400-600	1	W/F=1.05 mg min ml^{-1}	20	20-70	10-60	[66]
Ni/ La_2O_3-Al_2O_3	400-600	1	W/F=1.05 mg min ml^{-1}	20	72-92	46-70	[66]
Ni/Al	400-750	1	0.12 WHSV=50000 mL g^{-1} h^{-1}	20	85-95	0.4-4.4	[67]
Ni/modAl	400-750	1	0.12 WHSV=50000 mL g^{-1} h^{-1}	20	88-95	0.8-6	[67]
Ni/LaAl	450-750	1	0.12 WHSV=50000 mL g^{-1} h^{-1}	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]

ND: Not determined

WHSV: Weight hour space velocity

GHSV: gas hour space velocity

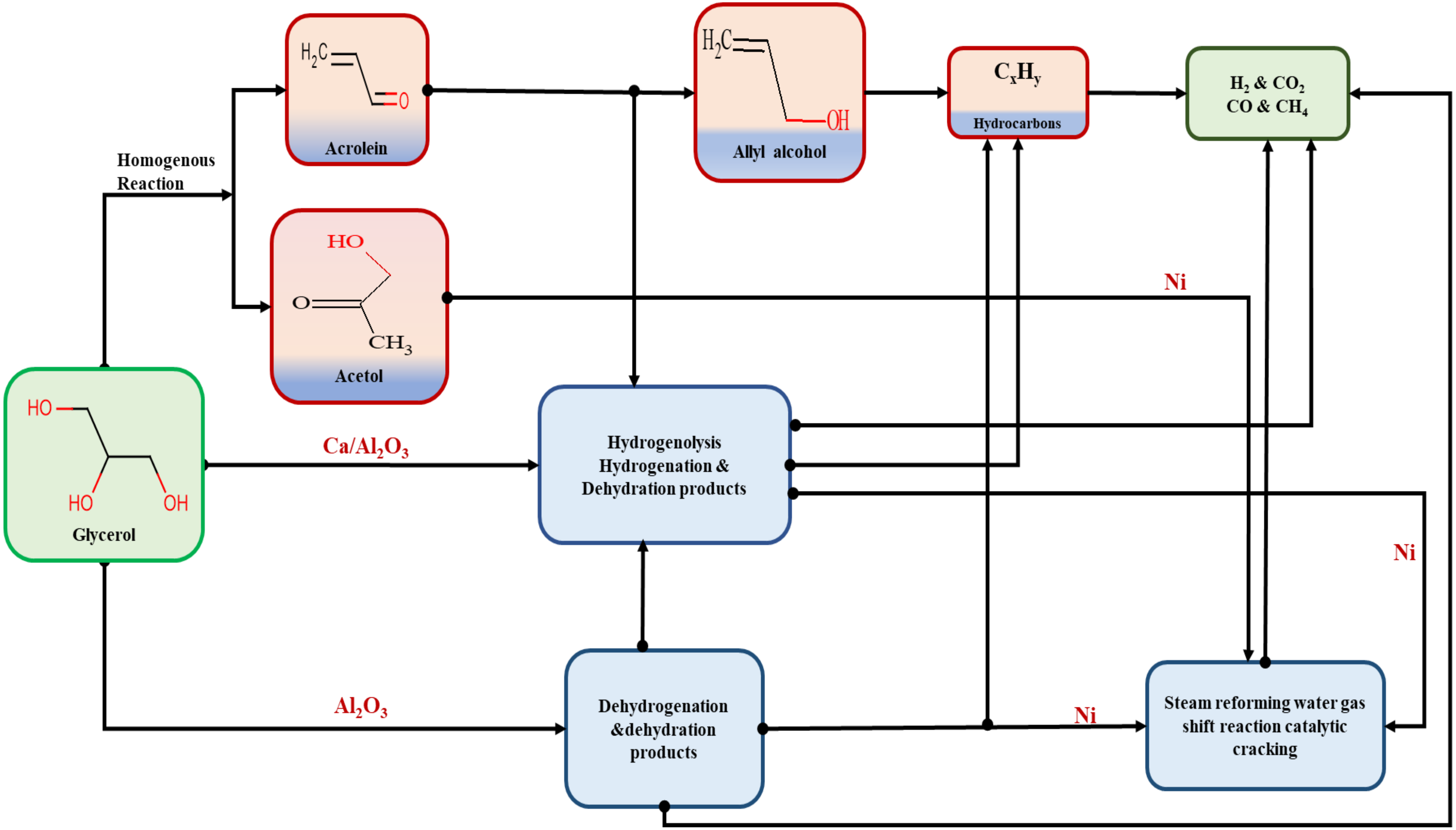


Fig.4. Proposed reaction pathway to the production of primary products in glycerol steam reforming over Ni based catalyst.

Conclusively, very few literatures are available for reforming of acetone for hydrogen or value-added chemical production. From above discussion it can be concluded that acetone conversion to hydrogen and other oxygenates mainly depends on metallic state, type of metal doping, acidity of support and reaction temperature. It can also be concluded that thermodynamic equilibrium for the reduction of acetone mainly depends redox potential and reaction temperature. Several reports highlighted the metallic interaction and significance of metal and support interaction for acetone reforming, and it can be concluded that Ni is essential part of catalytic design for acetone reforming. Whereas, several compositions such as Ni-Mo/Al_2O_3, Ni, Co, Mg, different Ni oxides, mixed oxide, spinel structure, NiZnO/CeO, Mn, Fe, Cu, Zn, Cu, CuPt and Pt have been investigated by different researcher. Conclusively, each metal behaved differently for reforming of acetone depends on their stability, coke formation, deactivation and synthesis design. Among all the reported metals Mn, Fe, and Zn were revealed as not significantly active for reforming of acetone. Whereas, Ni, Co, Pt, Cu were reported as more significant metals for acetone reforming for hydrogen production. Fig. 5 represented a general chemical reactions (resketched) occurs during glycerol hydrogenolysis as summarized by (a) Miyazawa et al. and (b) Bildea et al [70,71].

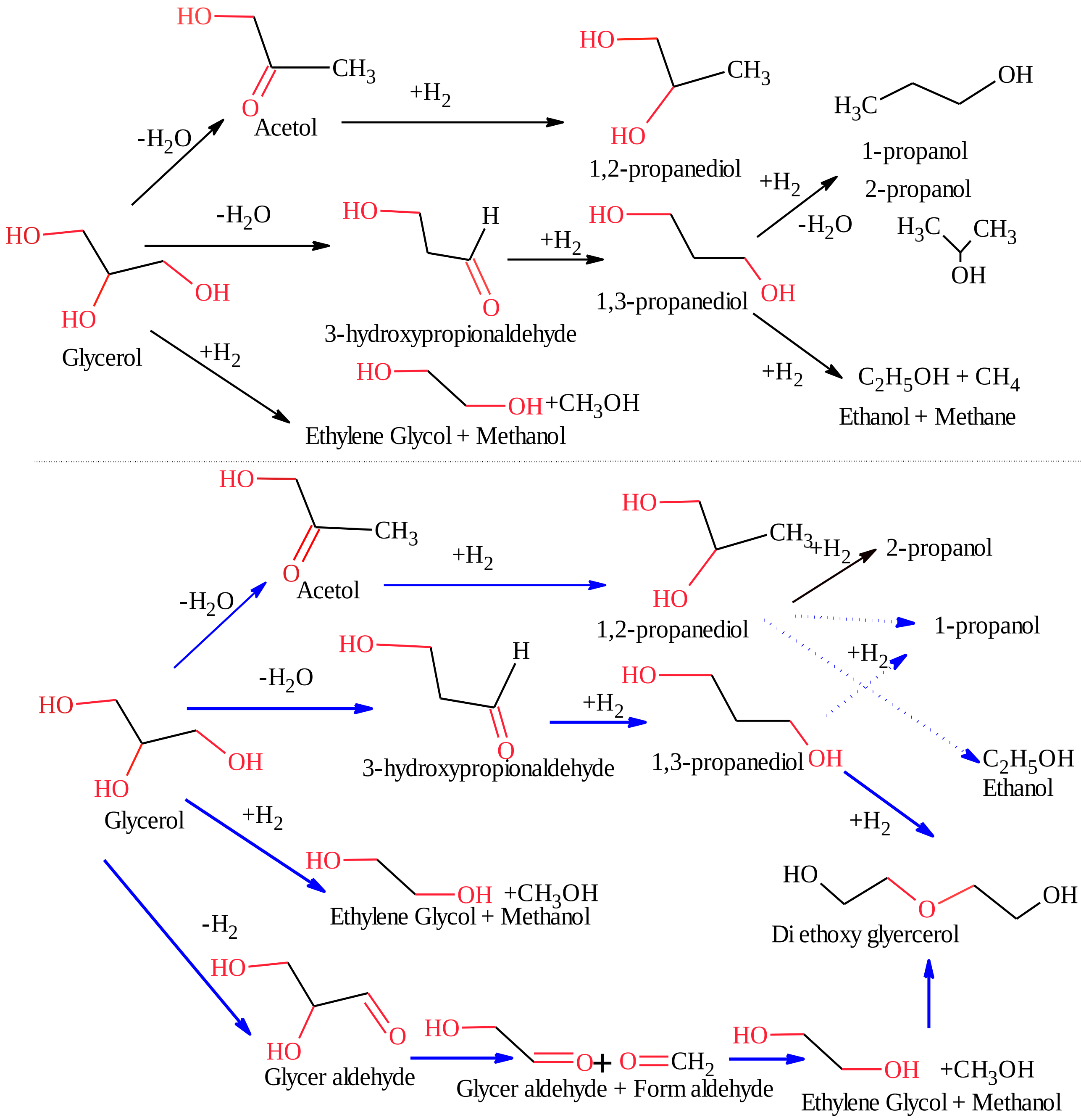


Fig. 5. Chemical reactions occurs during glycerol hydrogenolysis as summarized from (a) Miyazawa et al. and (b) Bildea et al. [70,71].

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

2.4. Autothermal Reforming

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

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

$$C_xH_yO_z + [2x-(z+1)]H_2O + \frac{1}{2}O_2 \rightarrow xCO_2 + \frac{2[2x-(z+1)]+y}{2}H_2 \tag{23}$$

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

Partial oxidation:

$$C_2H_5OH + \frac{1}{2}O_2 \rightarrow 2CO + 3H_2 \tag{24}$$

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

$$C_2H_5OH + \frac{1}{2}O_2 + 2H_2O \rightarrow 2CO_2 + 5H_2 \quad (25)$$

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

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

Veiga et al.[69] investigated the production of hydrogen rich gaseous mixture from steam and oxidative reforming of crude glycerol over Ni (12 wt.%)-$La_2(Ce1\text{-}xZrx)_2O_7$ (x=0, 0.5, 1). The catalysts were prepared by polymerized complex method based on the reaction route. The steam reforming was performed at 650ºC in fixed bed reactor with feed 30wt.% glycerol solution. The catalysts with highest basicity (Ni-$La_2(Ce0.5Zr0.5)_2O_7$ was proven to be the best catalyst in terms of activity. Oxidative steam reforming was successfully achieved with highest hydrocarbon yield over all the catalysts. Whereas, the catalyst containing both Ce and Zr showed best catalytic performance for hydrogen production and low deactivation of the catalyst.

2.5. Dry Reforming

Dry reforming, also known as carbon dioxide reforming, is a reforming reaction between oxygenates and carbon dioxide to produce syn gas, i.e. hydrogen and carbon monoxide. To date, in comparing among all oxygenates selected; only ethanol has been researched so far in the context of dry reforming [88,89]. Although research on carbon dioxide reforming of ethanol, known as dry reforming of ethanol (DRE), is not as established as SRE and ATRE, there is a growing interest in this reforming technology due to cheap reactant costs and a commitment to the reduction of CO_2 in the environment, hence converting the syngas into a valuable product [39]. DRE is a strongly endothermic reaction (ΔH^o_{298K}= 296.7 KJ/mol). The stoichiometric reaction of DRE is as follows:

$$C_2H_5OH + CO_2 \rightarrow 3CO + 3H_2 \tag{27}$$

However, the above reaction needs to be carefully controlled since there are many competitive side reactions taking place, such as dehydrogenation of ethanol to acetaldehyde, dehydration of ethanol to ethylene or decomposition of ethanol into CO, CO_2 or acetone. Thus, enough CO_2 supply is highly crucial to ensure optimum H_2 production. DRE may take place between 500 – 1100ºC with the optimum range reported to be between 950 – 1050ºC. It is important to operate DRE at a high temperature to reduce coke formation, and, ultimately, high H_2 selectivity [39].

In recent studies another experiment was designed by Moretti et al. [90] to study the ethanol steam reforming by using Nickel and bimetallic Ni-Co supported on ceria zirconia mixture. The investigation revealed that ceria and zirconia facilitated the metal oxide reduction of metal supported oxide phases. Among all the reported catalysts formulation Moretti et al. [90] suggested the CZ91NiCo catalysts showed the high ethanol conversion to hydrogen and selectivity towards CO_2 was found to be more than 500°C [90]. Recently, our studies showed that the 15% of NiCaO give the highest hydrogen yield and glycerol conversion that peaked at 24.59 % and 30.32% [91].

2.6. Partial Oxidation

Partial oxidation is another reforming technology to convert the oxygenated hydrocarbons into hydrogen and CO_2 or syn gas. In this reforming technology, the reaction is exothermic in nature, where it is not required to provide external heating other than the supply of air or pure oxygen. Complete oxidation (air supply in excess) will burn the fuel or reactant completely, hence reducing the amount of hydrogen produced. Therefore, the amount of air or oxygen supplied may need to be carefully controlled to yield the optimum products. The stoichiometric equation of partial oxidation is as follows and applies to all oxygenates:

$$C_xH_yO_z + \frac{(2x-z)}{2}O_2 \rightarrow xCO_2 + \frac{y}{2}H_2 \tag{28}$$

In order to obtain syn gas (CO and H_2), ethanol and propylene glycol would require ½ mol of oxygen additionally, which is less than what is required for conversion to CO_2 and H_2. However, ethylene glycol and glycerol stoichiometrically would not require any additional air to decompose into syn gas as both O/C ratios are

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

2.7. Aqueous Phase Reforming

Aqueous phase reforming [99], also known as hydrothermal reforming, is the reforming in an aqueous phase. This is a reforming technology that operates in excess water content, at lower temperature (generally between 200 – 300ºC) and high pressure up to 60 bars. APR is highly suitable for oxygenated hydrocarbons, mainly polyols, due to the presence of oxygen that weakens the C-C bond, and thus allows for easier splitting between hydrogen and CO. CO could further undergo the water gas shift reaction to be converted to CO_2 [100]. However, for the case of typical hydrocarbons, which only contain C & H atoms, the bonding energy is greater, hence APR is not an attractive choice. Fig. 6 shows a typical reaction pathway for reforming technology using various renewables raw materials such as bio-oil, carbohydrates and bioethanol for hydrogen production.

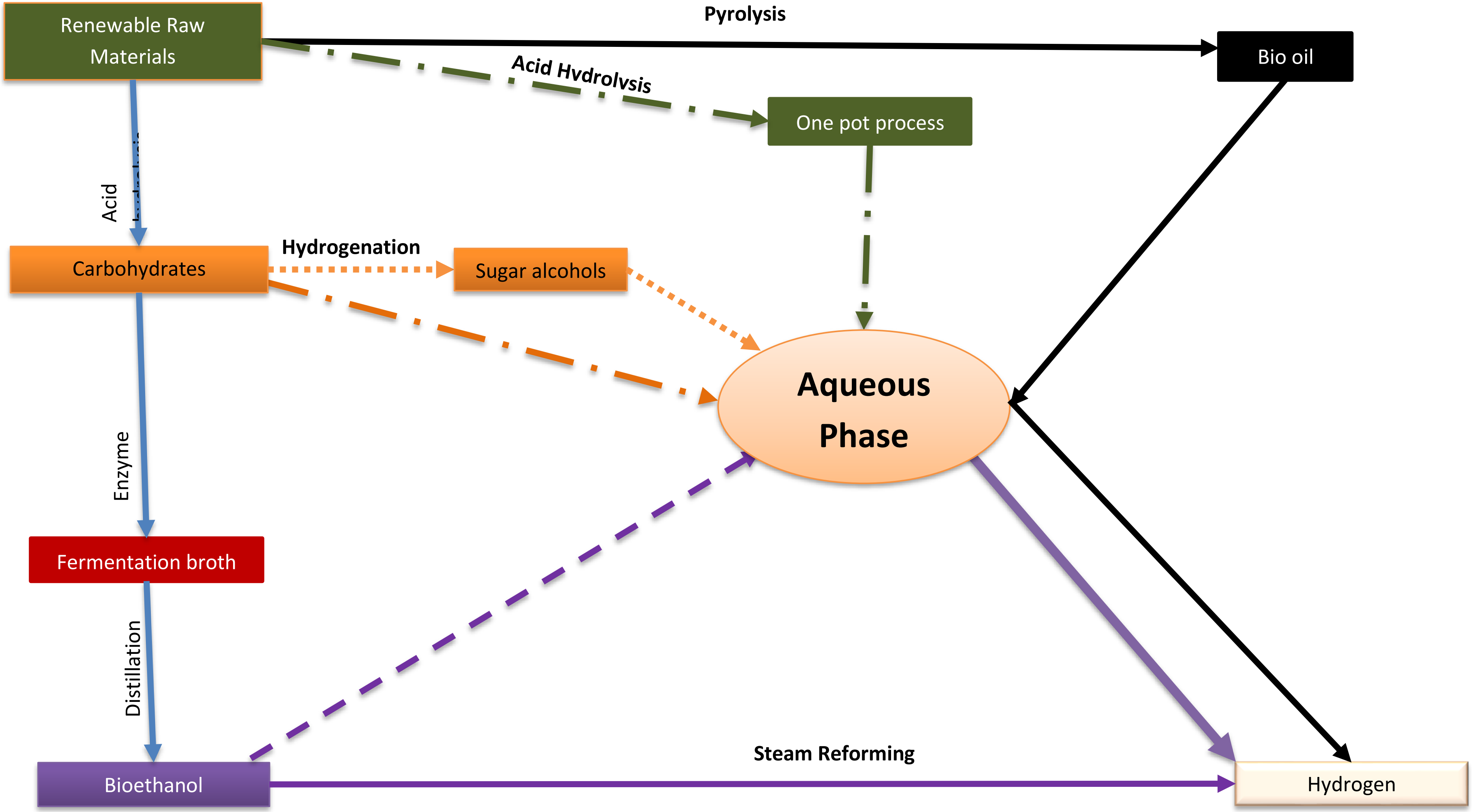


Fig 6. A summary of hydrogen production using reforming technologies.

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

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \tag{29}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{30}$$

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

Similarly, the thermodynamic studies of glycerol was carried out by Seretis et al. [105] via aqueous phase reforming using the Gibbs free energy minimization method. Seretis et al investigated the effects of different parameters such as water to glycerol mass ratio (W/G =4-14), temperature (3 - 227^{o}C) and pressure ratio P=P sat H_2O ¼ 1−2 for production of hydrogen, methane and carbon. The critical investigation suggested glycerol conversion reached up to 100% with hydrogen selectivity up to 70% under the broad-spectrum examination conditions. Under the similar conditions the methane formation was observed to be less at low pressure and high temperature. Since the reported results showed that methanation was thermodynamically preferred over hydrogen production. Beside this, it was also observed that glycerol conversion into carbon was found to be up to 80%. From all the investigation Seretis et al. [105] suggested that carbon can be eliminated at pressure ratio P=P sat H_2O ≤1:4 and temperature values T N 126.85 ^{o}C. The overall conclusion for all investigation suggest that the optimal W/G for H_2 production was found equal to 9 under thermodynamic equilibrium conditions [105].

3. Catalyst development

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

3.1. Transition metal catalyst

A common non-noble metal catalyst that is usually used is nickel, which has been long established for natural gas reforming, with alumina (γ-Al_2O_3) as its support [106]. However, oxygenates can easily dehydrate and form ethylene, which can pose serious coking problems by undergoing polymerization that is promoted by the acid sites of alumina [107]. Ethanol steam reforming via Ni/Al_2O_3 was also studied by several researchers[108-110], mainly to investigate any possibility of modification in catalysts formulations .

As for glycerol, a Ni-based catalyst has also been widely used in much of the research. Sanchez et al. [111], Adhikari et al. [112] and Cheng et al. [113] demonstrated steam reforming of glycerol using a Ni-catalyst. Sanchez et al. and Cheng et al. worked on a Ni/Al_2O_3 catalyst. Both findings agreed that coke formation is inevitable with this type of catalyst. Sanchez and colleagues focused on a Ni catalyst with Al_2O_3 as support and operating at a very high steam to fuel ratio (16:1) to avoid possible dehydration. Based on the Temperature Programmed Reduction (TPR) analysis, Ni- in Al_2O_3 existed within three states: (i) Bulk or free NiO (< 400ºC) [114] NiO bonded to Al_2O_3 (between 400 and 690ºC) and (iii) NiO incorporated into Al_2O_3, i.e. formation of $NiAl_2O_4$ (> 700ºC). The formation of $NiAl_2O_4$ may result in a difficulty to reduce the nickel prior to the reforming reaction. They further concluded that the catalyst deactivation was associated with the increase in the weight hourly space velocity (WHSV), i.e. operating at low catalyst loading, hence affecting the hydrogen selectivity. However, the changes of temperature (within range of 600–700ºC), did not significantly affect the hydrogen selectivity. Nevertheless, a stable catalyst can be achieved for a longer period at a higher operating temperature.

Researchers have focused on selectivity of catalysts towards the hydrogen production from various oxygenates, glycerol is one of them for steam reforming. Similarly, Sad et al. [115] recently investigated Pt based catalysts for glycerol steam reforming reaction for production of hydrogen. As the steam reforming reaction based on two steps firstly decomposition of glycerol and secondly water gas shift reaction (WGS). Sad et al. [115] tested Pt supported by different physiochemical properties catalysts (SiO_2, MgO, Al_2O_3 and TiO_2) for steam reforming of glycerol (10 wt.% aqueous solution). The reaction carried out at the temperature range of 300-350ºC. The glycerol conversion was found to be 100% with 78.8% hydrogen yield over Pt/SiO_2. Acidic support like Al_2O_3

and MgO favored the adverse reaction directing towards the liquid product and coke precursors. Sad et al. [115] reported the water gas steam reaction at compatible reaction conditions over Pt/SiO_2 and Pt/TiO_2 and Pt/CeO_2 and Pt/ZrO_2 were found with highest CO conversion at 350ºC. They also tested the double bed catalytic system of 0.5 wt. % Pt/SiO_2 and 0.5 wt.% Pt/TiO_2 to study the effect on hydrogen production. It was observed that by using double bed catalytic system the hydrogen yield increased up to 100% without deactivation on stream [115].

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

Doukki et al. [117] investigated the glycerol steam reforming over Ni and NiPt/γ-Al_2O_3 catalysts in aqueous phase reforming for hydrogen production. Doukki et al. [117] actually investigated the hydrothermal stability of the catalysts that were prepared with different preparation methods i.e. solgel in basic medium and impregnation on an in-house sol gel γ-Al_2O_3 support. After the detail investigation on characterization Doukki et al. [117] revealed that sol gel impregnation method was found to be crucial in extending the catalyst life due to adequate distribution of Ni-Pt metallic particles and good thermal stability of γ-Al_2O_3 for aqueous phase reforming process. Whereas, Sol gel basic catalyst exhibited homogenous dispersion of Ni particles but unstable to show good catalytic behaviour. Among all the formulations of catalysts ASGI (Alumina SolGel Impregnation) the activity was reported as NiPt/ASGI7>NiPt/ASGI6 > NiPt/ASGI5 > NiPt/ASGB7). NiPt/ASGI7 showed good catalytic activity with stability of 56 hours of time on stream with highest glycerol conversion of 79% and gaseous products of 57% for hydrogen production.

In the same way, Dou et al. [118] investigated the effect of H_2S and HCl impurities in steam reforming of naphthalene over synthesized Ni and Fe supported over alumina catalysts and commercial catalysts. The purpose of the study was to investigate the poisoning effect of HCL and H_2S on catalysts. Steam reforming was performed over 790, 850 and 900°C over synthesized and commercial catalysts. Dou et al. [118] revealed that there was no significant effect of Fe addition on steam reforming and water gas shift reaction. The main effect on catalytic behavior was mainly due to generation of active sites by H_2S and HCl. He further reported that H_2S

mainly effects the reforming of naphthalene compared to HCl. Similarly, poisoning was also affected by H_2S not by HCl. H_2S chemisorbed on Ni surface catalysts and forms NiS and start to decrease the active sites available for hydrocarbons in steam reforming. Whereas, poisoning for water gas shift reaction was affected by both H_2S and HCl, and activity was completely restored by removal of H_2S and HCl from gas. Dou et al. [118] further reported that H_2S poisoning can be prevented by performing reforming reaction at higher temperature for naphthalene. The increase of temperature 790°C to 900°C increased the naphthalene conversion from 40% to 100%. Whereas, poisoning of water gas shift reaction of reforming of naphthalene was significantly influenced by the structure of the catalyst. Dou et al. [118] findings revealed that strong binding energy between Ni and alumina support significantly influenced the minimum loss of water gas shift reaction.

Recently Arregi et al. [119] investigated the renderability of commercial Ni catalyst used in steam reforming of volatiles from pyrolysis of biomass for hydrogen production in successive regeneration cycles. Catalytic activity for steam reforming was not fully enclosed by coke combustion in first cycle mainly due to deactivation of Ni sintering but the catalyst reached a pseudo-stable state further from fourth cycle, repeating its behavior in following cycles. The commercial catalyst was reported as highly active and selective for hydrogen production. The conversion and hydrogen yield at initial time on stream decreased from first to the sixed cycle, from 99.7-90.1% and from 93.5 to 72.4% respectively. Fig. 7 shows a general representation of active metal sites of Ni-Ca/ Al_2O_3 catalyst in GSR reactions.

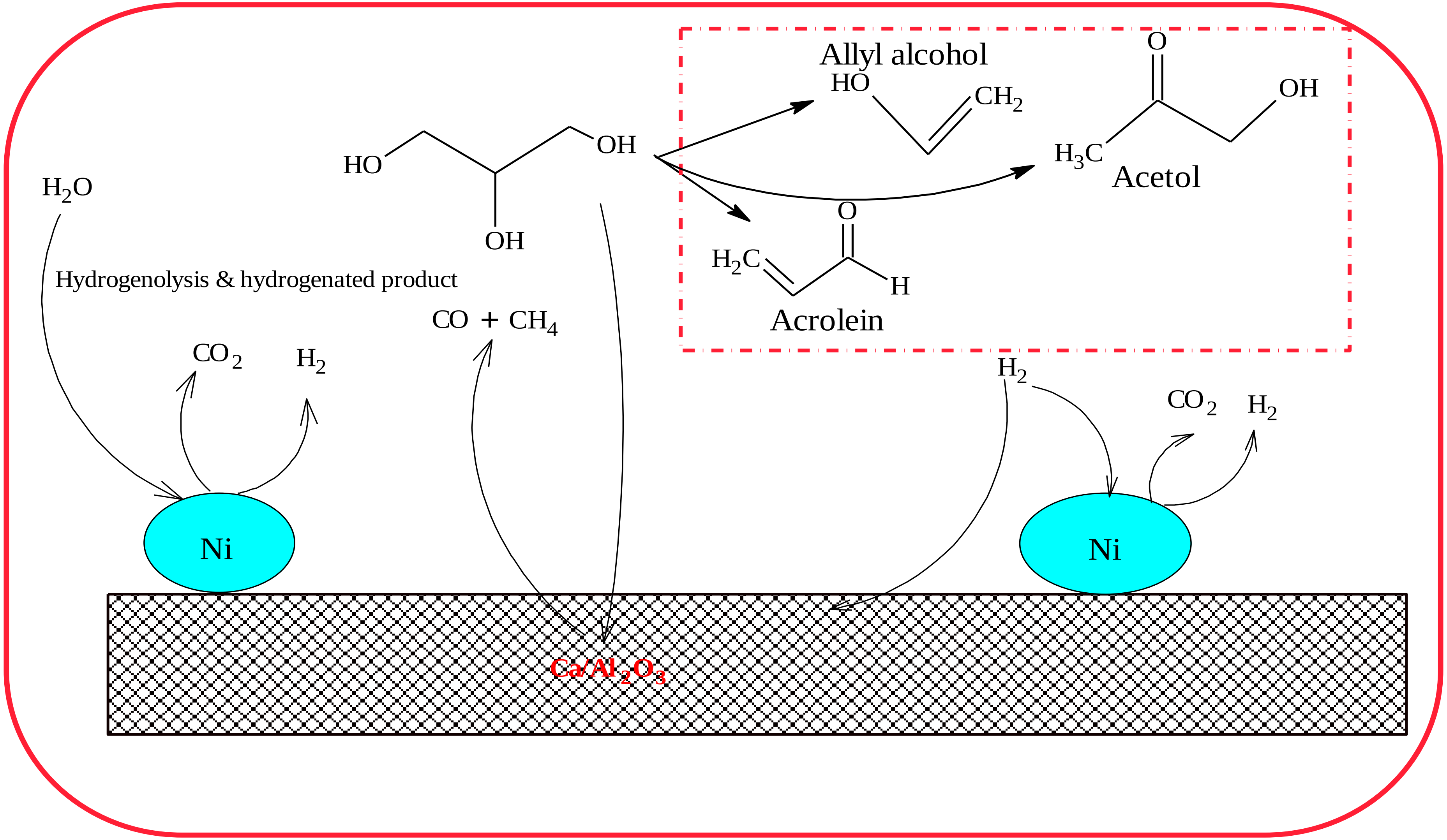


Fig. 7. Schematic of Ca doped Nickel alumina surface activity from glycerol steam reforming reaction.

3.2. Noble Metals and Other Catalysts

Apart from nickel[120], noble metal catalysts such as Rh[48], Ru[121], Pt[122], Pd[123], and Ir[124] have also been widely investigated. It was claimed that the Rh catalyst is among the most efficient catalysts for the reforming process as experimented by Cai et al. [82]. Though, alumina as an excellent support, CeO_2 is another support that has gained high interest. CeO_2 is claimed to be a better promoter that can lead to higher dispersion of metal particles and strong interaction between the metal and the support. Improved stability has also been reported [125]. However, a frequent start-up and shutdown of the system may lead to the γ-CeO_2 deactivation due to the formation of carbonate on the surface of the catalyst [126]. The use of noble metals has also been reported by several authors in either ethylene glycol or glycerol reforming technologies, such as Dauenhauer et al. [127] on autothermal reforming of both components (Rh, Rh-Ce, Rh-La, Pt with ceramic as support), and Chiodo et al. [48] on the comparison of Rh- with Ni- performance on glycerol steam reforming.

Lately, Ramesh et al. [128] further studied the steam reforming of glycerol to hydrogen at low temperature by using copper decorated perovskite catalysts under the reaction condition of vapor phase. In comparative studies of all catalysts, $LaNi0.9Cu0.1nO_3$ showed best conversion (73%) of glycerol and selectivity for (67%) hydrogen. The catalyst characterization was performed before and after the reaction. During the TPRO-H_2, it was observed that perovskite structure decomposed to La_2O_3, Ni and Cu. The nano particles were generated by the deposition of Cu on Ni. The decoration of Cu increased the reduction of active Ni species with adequate basicity. It was observed that the activity of catalysts decreased with increment of Cu concentration. ($LaNi0.9Cu0.1O_3$) was found to be active till 24 h at 650ºC. The researchers observed that TGA analysis showed that the copper decorated catalysts have enough resistance for coke formation as compared to perovskite catalysts. It was determined by the authors that the accumulation of copper in perovskite oxide and generation of Cu/Ni nano particles enabled the dehydrogenation and decomposition of glycerol in steam reforming [128].

Li et al. [129] performed the ethanol steam reforming over BaZr0.1Ce0.7 Y0.1Yb0.1O3ed catalyst over Ni supported catalysts [129]. The catalyst is reported for 100% conversion into various gaseous products such as H_2, CO, CO_2 and CH_4 depending on reaction temperature range between 500-750ºC. The hydrogen yield of hydrogen and CO was reported as 85% only for the reaction carried out below 600ºC and decrease to 80% at 650ºC and 750ºC. Li et al. [129] stated that methane amount below 10% at all temperatures. By decreasing hydrogen to ethanol ratio from 5 to 3 results in several percent increase for CO and decrease for hydrogen and CO_2.

Huang et al. [130] performed the glycerol steam reforming over Ni/Al_2O_3 catalyst with addition of Ca-Mg and La-Ce-Zr oxides as support exhibit the excellent catalytic activity for higher production of syngas. Huang et al. [130] reported CO_2 <2.8% and methane (0.07%) in syngas produced via glycerol steam reforming. Author also reported that reforming gas $(H_2\text{-}CO_2)/(CO+CO_2)$ molar ratio was determined approximately 2.09. Author introduced methane in glycerol steam reforming system in order to inhibit the CO_2 production through dry reforming. The optimized condition for syngas yield was determined as 87.7% on glycerol conversion, that was much higher than that in glycerol steam reforming without methane.

Recently Remiro et al. [131] reported the deactivation mechanism of commercial catalyst $Rh/CeO_2\text{-}ZrO_2$ for steam reforming of raw bio-oil. Moreover, regeneration, reusability and reason for deactivation of fresh and regenerated catalysts was also investigated in detail. Steam reforming was followed by pyrolysis oil in two unit in series as reactor under suitable temperature. Remiro et al. [131] reported that structural changes were irreversible and occurred rapidly. The deactivation selectivity affects the reforming of oxygenates from lowest to highest reactivity. Rh sintering was not significantly cause deactivation at reaction temperature; it was an unindustrialized deactivation cause at (700ºC).

3.3. Effect of promoters

Promoters are usually added to the catalyst for modifying the catalytic support structure, and, hence, the electron distribution property within the catalyst system to enhance its reaction performance. However, using it alone had no catalytic effect on the reaction. Among the promoters that have been tested since las decade for the purpose of research in reforming works were: Ca [132], Mg [133,134], Gd [135], Nb[136] , Zr [137], and La [138]. The research work on group II-doped catalysts on oxygenated hydrocarbons reforming is one of recent interest. Due to its basicity, doping with calcium and magnesium is hypothesized to be able to reduce the acidity of alumina as support; hence, inhibiting the dehydration of oxygenates that lead to the formation of ethylene. The research works associated with promoting calcium to Ni/Al_2O_3 were carried out by Choong et al. [132], Elias et al. [139] and Vizcaino et al. [140] on ethanol steam reforming. Vizcaino et al. also studied on Mg addition to Ni/Al_2O_3 [140]. A comprehensive literature is tabulated in Table 2 based on transition metal and noble metal catalysts for oxygenates reforming.

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

Feedstock	**Catalyst**	**Temp (ºC)**	**$C_2H_6O/H_2O/O_2$ (molar ratio)**	**xC_2H_6O (%)**	**SH_2(%)**	**Ref**
Bioethanol	Ni/CeO_2-ZrO_2 $RhNi/CeO_2-ZrO_2$	600	1:9:0.35	91-100	3.5-4.6	[141]
Ethanol	Ce:Zr = 9:1) Nickel, Cobalt, Nickel-Cobalt (CZ91NiCo)	250-750	1:6	90	80	[90]
Ethanol and Methanol	(Ni, Cu, Ru, Pt) and bimetallic (Pt-Ni, Pt-Cu, Pt-Ru/ detonation nanodiamond (DND)	150-650	1:1 (for MSR) or 1:3 (for ESR)	High	High	[142]
Bioethanol	$Ni/La_2O_3-Al_2O_3$ and $Ni/CeO_2-Al_2O_3$	150-350	43.69 g/L	90	63.6	[143]
Ethanol	18 wt% Ni /$\alpha-Al_2O_3$, 25 wt% Ni/$\alpha-Al_2O_3$	600		78	17	[144]
Methanol	Cu/Zn/Al/Zr/ porous copper fiber sintered felt (PCFSF)	240-400	GHSV 16,252.4 ml/g h).	90	high	[145]
Bio-oil	Ni-Co/Al-Mg	650	S/C ¼ 12 mol/mol, Liquid flow rate ¼ 0.12 mL/min,	high	0.101 to 0.182 g H_2	[146]
Bio-oil	$Ce-Ni/Co/Al_2O_3$	700	LHSV of 0.23 $h^{–1}$	94.1	83.8	[147]
Methanol	$Cu/Zn-Al_2O_3$	200-350	ND	51.87	75.4	[148]
Acetic acid	$Ni/Ce_{0.75}Z_{0.25}O_2$ $Co/Ce_{0.75}Z_{0.25}O_2$	450-650	WHSV=134h^{-1}	100	High	[34]
Bio-oil	$Ni/CeO_2-Al_2O_3$ $Rh-Ni/ CeO_2-Al_2O_3$ $Ru-Ni/ CeO_2-Al_2O_3$	800	S/C=5 WHSV=21.15h^{-1}	100	High	[149]

Ethylene glycol	5 wt% Ni/Al_2O_3	600	1:9	36	20	[150]
	3.75 wt% Ni-1.25 wt% Pt/Al_2O_3			60	44	
	2.5 wt% Ni-2.5 wt% Pt $/Al_2O_3$			50	40	
	1.25 wt% Ni-3.75 wt% Pt $/Al_2O_3$			40	30	
	5 wt% Pt/Al_2O_3			30	30	

ND: Not determined;C_{Feed}: Feed conversion; SH_2: Hydrogen selectivity

This is justified from the literature that the catalyst plays an important role in hydrogen production via steam reforming. Hammoud et al. [148] recently studied the synthesis of copper supported on calcined hydrotalcite catalysts using the resulting effect of Zn-/Alumina hydrotacite. The steam reforming reaction was carried out in a fixed bed reactor under the mild conditions at the temperature of 200-350ºC. The physiochemical properties were identified in result of characterization technique. From the experimental database of Hammoud et al. [148] it was evaluated that 10%Cu/Zn-Al showed higher activity (75.44%) of hydrogen was produced with 51.87% of methanol conversion at 250ºC. It was confirmed from the experiment that methanol conversion was found to be strong function of catalysts reducibility and copper concentration. The activity of catalysts like Cu_2O also depends on temperature provided [148]. In our recent studies we reported the CO_2 dry reforming of glycerol for syngas production. The dry reforming was performed using Ag promoted Ni-based catalysts supported on SiO_2, the reaction was performed in tubular reactor at 700ºC and CO_2: glycerol ratio of 1, at ambient pressure. The gaseous products such as H_2, CO, and CH_4 with H_2: CO < 1.0 were included in our findings. The detail reaction studies revealed that $Ag_{(5)}NiSiO_2$ showed outcomes in highest glycerol conversion and hydrogen yield, accounted for 32.6% and 27.4%, respectively [151].

Bastan et al. [152] also examined the effect of promoter over a series of Ni nano catalysts supported with alumina and MgO for aqueous phase reforming of glycerol in order to determine the optimum catalysts for hydrogen production. Bastan et al. [152] revealed that the APR activity mainly depend on catalysts promotor ratio. Furthermore, catalytic activity of NiMgO and Ni/ Al_2O_3 for both were lower than their corresponding mixed oxides and catalytic activity increased with Al/Mg ratio. Bastan et al. [152] reported conversion of glycerol (92%) and hydrogen selectivity (76%).

Aqueous phase reforming of crude glycerol was conducted by Larimi et al. [83]. Over 5wt.% PtM/Al_2O_3 i.e. (M ¼ Pd, Rh, Re, Ru, Ir, Cr) catalysts for hydrogen production. Larimi et al. [83] reported that the catalytic performance mainly depend on both active metal loading and type of promoters. Among all the formulations 5 wt.% Pt loading with Rh/ Al_2O_3 was observed to be the best for the catalytic activity for hydrogen production rate 42625 mmol/gcat h^{-1}) and selectivity of (89%) in APR of 10wt.% pure glycerol solution.

Phongprueksathat et al. [34] performed the catalytic steam reforming of acetic acid over Ni, Co supported by Ce-Zr oxide at reaction temperature of 450-650ºC. The author reported that Ni/$CeZrO_2$ and CoCeZrO were found to be potential catalysts to activate the Ce-C bond cleavage and reforming of cracked intermediates. He found Ce-ZeO_2 (CZO as an active support in steam reforming of acetic acid that favours the ketonization reaction rather than C-C bond cleavage reaction at lower temperature. He reported that Ni/CZO catalyst was more active for acetic acid steam reforming due to higher Ce-C bond cleavage activity than Co-CZO catalysts.

3.4. Catalysts preparation methods

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

Neto et al. [154] studied on the effect of preparing Ni based catalysts supported on γ-Al_2O_3 using three different methods which are nanocasting (NiAlN) , co-precipitation(NiAlC) and incipient wetness impregnation(NiAlW) for glycerol dehydration reaction. It was found that different catalyst preparation method possesses different physicochemical properties of the catalysts. NiAlN exist in mesoporous structure with the highest specific area and pore size compared followed by NiAlW and NiAlC which both exist in micropores structure. The XRD results obtained shows that NiAlC has the highest peak of cubic phase which indicate high crystallinity of the catalyst compared to NiAlN and NiAlC catalysts. The performance of the catalysts evaluated for dehydration of glycerol shown that NiAlW had the highest catalytic performance with 19.7% glycerol conversion and no catalysts deactivation during the reaction. However, the performances of NiAlN and NiAlC decreased with glycerol conversion of only 3.3% and 8% respectively due catalyst deactivation. Table 3 presents various methods of catalysts preparation implemented in reforming technologies. There is still a huge gap to be focused on catalysts preparation method and study the physicochemical properties on various applications.

Table 3. Catalysts preparation method for reforming process.

Catalyst	Preparation method	Reforming technique	Feed	Operating condition			Results		Ref
				Temp (ºC)	Pressure (atm)	Feed conc (wt%)	C_{Feed} (%)	SH_2 (%)	
Ru/γ-Al_2O_3	Wet co-impregnation	Steam reforming	Glycerol	400-800	1	20	35-92	High	[155]
Ru/B_2O_3-Al_2O_3	Wet co-impregnation	Steam reforming	Glycerol	400-800	1	20	15-85	High	[155]
Ru/MgO-Al_2O_3	Wet co-impregnation	Steam reforming	Glycerol	400-800	1	20	20-55	High	[155]
2 wt% Mo/Al	Sol-gel	Steam reforming	Glycerol	400-500	1	10	10-40	42-55	[156]
5 wt% Mo/Al	Sol-gel	Steam reforming	Glycerol	400-500	1	10	15-40	40-50	[156]
12 wt% Mo/Al	Sol-gel	Steam reforming	Glycerol	400-500	1	10	18-50	35-45	[156]
10 wt% Ni/ CeO_2	Co-precipitation	Aqueous phase reforming	Glycerol	250	25	10	62	85	[120]
10 wt% Ni/ $Ce_{0.7}Zr_{0.3}O_2$	Co-precipitation	Aqueous phase reforming	Glycerol	250	25	10	87	66	[120]
10 wt% Ni/ ZrO_2	Co-precipitation	Aqueous phase reforming	Glycerol	250	25	10	55	79	[120]

12Ni-1Cu/MWNT	Sonochemical method	Aqueous phase reforming	Glycerol	240	40	10	84	86	[157]
Pt (2.77wt%)/ Al_2O_3	Incipient wetness impregnation	Aqueous phase reforming	Glycerol	225	29.3	10	ND	31	[158]
Ni/Al_2Mg	Co-precipitation	Aqueous phase reforming	Glycerol	250	50	10	92	76	[152]
Pt/Al_2O_3	Incipient wetness impregnation	Aqueous phase reforming	Glycerol	225	29	10	ND	17	[159]

ND: Not determined;C_{Feed}: Feed conversion; SH_2: Hydrogen selectivity

4. Merits and Demerits

The renewable and sustainable energy system has been developed in the last few decades. To develop the most promising clean system, energy produced from hydrogen has been targeted for an interest of many researchers. Hydrogen produced from glycerol and ethanol steam reforming are the most common among them. Glycerol is by-product of many industrial processes such as methyl and ethyl esters, soap and biodiesel production. The GSR process has been developed for hydrogen production on lab-scale because it does not need any further changes in industrial process based on steam reforming. The selection of catalysts for hydrogen production via GSR process is an important and fundamental need. Catalysts have been developed using various noble metal for hydrogen production in GSR process such as Rh, Ru, Pt, Pd and Ir. Although these expensive catalysts give good yield of hydrogen, but researcher are always interested in finding cheaper and highly active catalysts. Based on these results Ni based catalysts become significant in hydrogen production for many researchers. The Ni based catalysts are quite cheaper, highly active, and more stable and allow working at lower temperature. Nevertheless, in the last few decades great efforts have been put on for Ni-based catalysts with development of various promoters to enhance the catalytic performance. For any catalytic activity and efficiency, support must play an important role. The influence of support must be considered during the development of catalysts. The support as neutral shows higher thermal stability and lower coke formation. The proper promoter used and wt.% doped on support also necessary in order to enhance the catalytic activity and stability. This is still an interesting field to work for. Subsequently, further research needs to be done for this area, to ensure that the catalyst is active at lower temperature and stable for longer time utilization, without significant coking issues.

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

In order to deal with intensified process of GSR, the separation of CO_2 from H_2 within the same pot continuously while reacting can be a great deal. It has been found that the removal of CO_2 or H_2 from the reaction mixture, moves the thermodynamic equilibrium towards higher glycerol conversion and high H_2 yields, which obey the Le Chatelier's principle. However, other operating conditions such as temperature, WGFR, WHSV and pressure must be dealt carefully to achieve optimum outcome. The CO_2 emissions can easily be evaded through SEGSR, However, the new solutions combining with catalytic GSR within situ CO_2 and H_2 removal would be an interesting phenomenon that needs to be researched.

5. Conclusion

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

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

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

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

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