Recent advances in renewable hydrogen production by thermo-catalytic conversion of biomass-derived glycerol: Overview of prospects and challenges

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HIGHLIGHTS

- Huge amount of glycerol is produced as by-product during biodiesel production.
- Hydrogen production by thermo-catalytic conversion of glycerol is reviewed.
- The prospect and challenges of the various thermo-catalytic conversion of glycerol to hydrogen are identified.
- The future research outlook on hydrogen production by thermo-catalytic conversion of glycerol is discussed.

GRAPHICAL ABSTRACT

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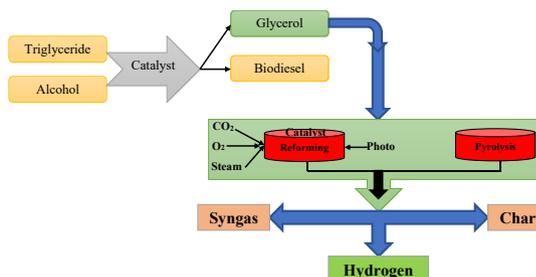
ABSTRACT

Glycerol is the main by-products obtained from the transesterification of vegetable oils and animal fats to produce biodiesel which is an important biofuel used for transportation. The increase in the global energy demand has pushed up the production of biodiesel with a corresponding increase in glycerol production over the years. The thermo-catalytic process is gaining wide popularity as sustainable technical routes of converting glycerol to renewable hydrogen. There exists a great potential of utilizing hydrogen as a critical part of a more sustainable and secure energy mix. Hence, this study focusses on the review of the recent advances and development in the thermo-catalytic conversion of glycerol to renewable hydrogen in the last one decade. The analysis of the reviewed articles showed that substantial efforts had been made in the application of thermo-catalytic process for

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Biomass
Glycerol
Reforming
Thermo-catalytic conversion

the conversion of glycerol to renewable hydrogen. Glycerol reforming using steam, carbon dioxide (CO_2) and oxygen (O_2) have received significant research attention and have been found to have great potential as technological routes for hydrogen production. Whereas, the use of the photocatalytic glycerol reforming has the advantages of energy-saving by utilizing the vast available solar resources and suitable photocatalysts. However, each of the thermo-catalytic processes exhibits inherent challenges which have been a bottleneck to the development of the process to industrial scales. Nevertheless, the prospect of employing each of the thermo-catalytic processes for hydrogen production via glycerol conversion was identified with the possible suggestion of strategies of overcoming the challenges.

Introduction

The quest for an alternative and cleaner source of energy is on the increase. This is primarily due to the adverse effect of global anthropogenic emissions of greenhouse gases through the combustion of fuel derived from fossil sources [1—3]. Several renewable energy sources such as wind, hydropower, solar energy, geothermal and bioenergy have been reported as viable and sustainable alternatives to conventional energy production from fossil fuel [4—7]. Based on the renewable energy policy network for the 21st century (REN 21) 2018 report, 279.8 billion USD was invested in renewable power and fuel [8]. Also, the reports show that modern renewable energy contributes 10.3% to the total global energy consumption for heat in 2017 while the traditional biomass contributed 16.4% for cooking and heating in the developing countries. Moreover, the share of renewable in the total global energy consumption for transport was put at 3.1% in 2017 [8]. Amongst the renewable energy understudied, biofuel which primarily consists of ethanol and biodiesel contributed the largest (2.8%) of the world energy consumption for transportation [8]. In 2017, 31 billion litres of Biodiesel was produced for transportation which accounts for 21.6% of the total fuel from the renewable energy source [8].

The production of biodiesel by transesterification of vegetable oils of animal fats is often accompanied by a huge amount of glycerol as the main by-product [9,10]. Due to the high demand for renewable energy for transportation purposes, studies have shown that the production of biodiesel will continue to rise which implies a corresponding increase in the glycerol production [11]. Although, glycerol has a wide range of applications in the chemical industries for making detergent, antioxidants, stabilizers, syrups, food supplements for animals and so on, it also has great potentials as a substrate that can be converted to high value chemicals such as lactic acid, ethylene glycol, dihydroxyacetone, and hydrogen [12,13]. Hence, glycerol has been projected as potential biomass-derived feedstock for the production of hydrogen and other value-added chemicals [14,15]. The utilization of glycerol as a substrate for hydrogen production is receiving overwhelming attention from the research communities as reflected in the number of articles published in the last 5 years (Fig. 1) [16—19]. This is due to the importance of hydrogen as a clean and efficient fuel with wide ranges of applications and can be used as an alternative fuel to fossil fuel in the future [20,21]. Amongst the different thermo-catalytic routes that have been investigated for glycerol conversion to hydrogen, steam reforming of glycerol received the greatest attention based on the number of articles published
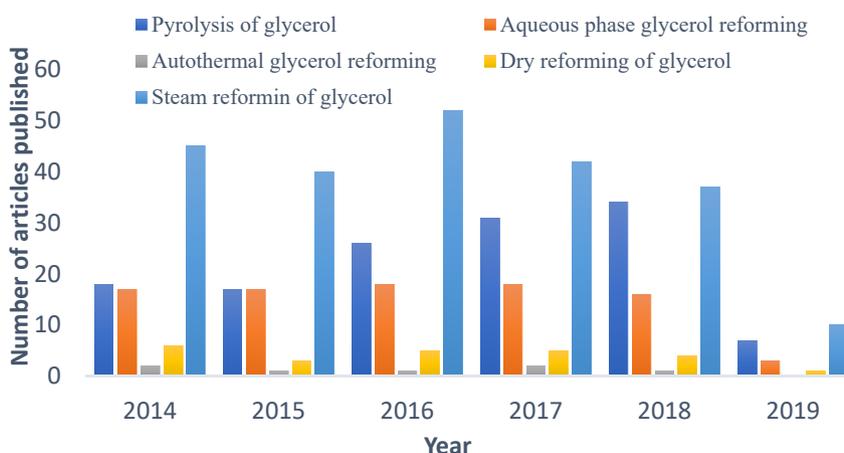
Fig. 1 — Comparison of the number of published articles on the different thermo-catalytic conversion of glycerol to hydrogen (Source: Scopus database).
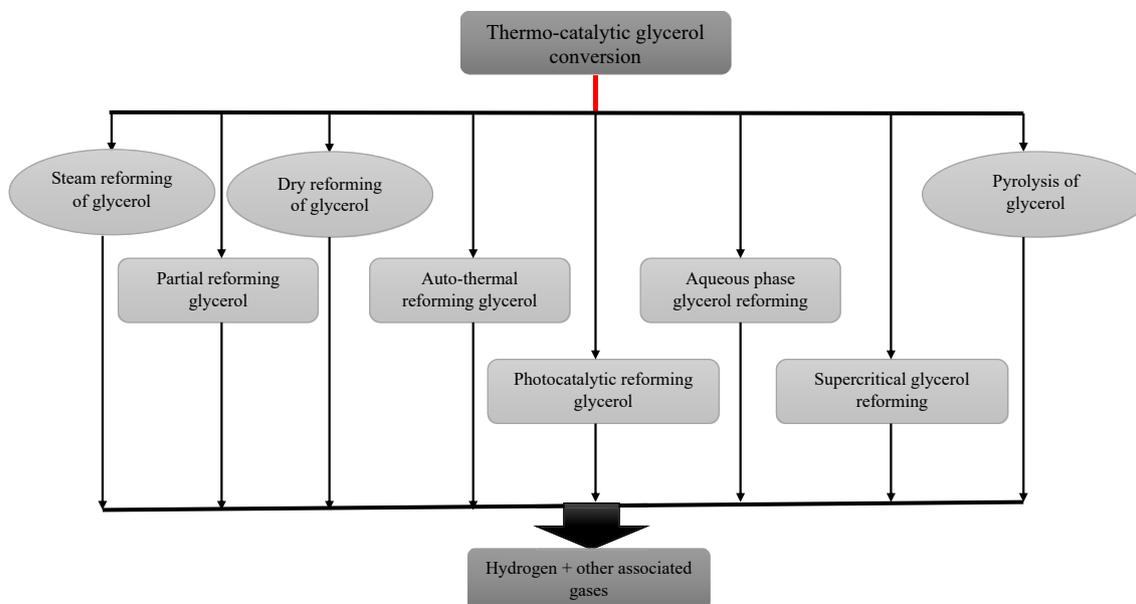
Fig. 2 — Schematic representation of the different thermo-catalytic conversion of biomass-derived glycerol to hydrogen.

in the last five years as shown in Fig. 1. On the contrary, auto-thermal glycerol reforming received the least research attention. Hydrogen is fast gaining wide acceptability as transportation fuel due to its potential in the zero-emissions of CO_2 and its high efficiency. Moreover, hydrogen can be used solely or combined with carbon monoxide and use as an important feedstock for the production of various value-added chemicals such as ammonia, methanol, oxygenates and Fischer-Tropsch fuels. In addition, hydrogen also finds wide application in various industrial processes such as metalworking, glass production, and electronics industries. In the petrochemical refinery, hydrogen facilitates the removal of sulphur from the crude oil during the refining of the crude oil to gasoline and diesel.

Several thermo-catalytic routes shown in Fig. 2 can be employed for the production of hydrogen from glycerol [22]. These thermo-catalytic routes involve the application of thermal energy and catalysts for the conversion of glycerol to hydrogen [23]. There are various review papers on hydrogen production from thermo-catalytic processes. Li-et al. [24] reported the production of hydrogen from several feedstocks such as wood, legume straw, apricot stone, rice husk and so on using thermo-catalytic processes. The authors analyzed literature related to the use of pyrolysis and gasification for the conversion of biomass to hydrogen. Muhammad et al. [25] and Ashik et al. [26] published review papers on hydrogen production by thermo-catalytic decomposition of methane mixed with hydrocarbons. The authors analyzed various literature related to metal-and carbonaceous-based catalysts used for thermo-catalytic conversion of methane to hydrogen. Korres and Norsworthy [27] in their book chapter presented an overview of biohydrogen production from agricultural biomass and organic waste. The authors reviewed the different biomass and organic waste-origin used for hydrogen production and their respective conversion processes. Markočič et al. [28] conducted a short review on hydrogen

production by supercritical glycerol reforming. The author reported the use of catalytic and non-catalytic supercritical glycerol reforming for hydrogen production. The present study differs from the previous review by focusing on the recent development in the use of thermo-catalytic processes for the production of hydrogen from glycerol. Moreover, literature related to the thermodynamic analysis and the kinetic studies of the hydrogen production by the thermo-catalytic glycerol conversion was reviewed and discussed. The innovations in the thermo-catalytic conversion of glycerol to hydrogen were also reviewed to identify the recent advances and to have an overview of the prospect and challenges which will serve as a guide for further studies.

Thermodynamic analysis of thermo-catalytic conversion of glycerol

Besides experimental investigations that have been reported on the thermo-catalytic conversion of glycerol to hydrogen, several studies exist on the thermodynamic analyses of glycerol dry reforming, glycerol steam reforming, aqueous phase glycerol reforming, and dry autothermal glycerol reforming [29—33]. These studies were investigated to thermodynamically analyze the effects of operating parameters such as the reaction temperature, partial pressure of the feed, and the molar ratio of the feed on the hydrogen production. Moreover, the effects of these parameters on carbon formation during the glycerol reforming process were also investigated.

Wang et al. [32] reported the thermodynamic analysis of hydrogen production by glycerol dry reforming using Gibbs free energy minimization method. The effects of CO_2 to glycerol ratio, temperature and pressure on the hydrogen production were examined. The thermodynamic analysis of the glycerol dry reforming revealed that operating the reactor at

higher pressure negatively influence hydrogen yield. Hence, operating the reactor at lower pressure favours higher hydrogen yield and glycerol conversion. The study also revealed that an increase in the reaction temperature resulted in a corresponding increase in the hydrogen yield which attained the maximum value at CO_2 to glycerol ratio of 2. On the contrary, the increase in the CO_2 resulted in a decline in hydrogen production which can be attributed to the effect of methanation side reaction. An optimum operating condition of 727 °C, CO_2 to glycerol ratio of 1 and atmospheric pressure was proposed for minimization of carbon deposition during the glycerol dry reforming. In a similar study, Kale et al. [30] reported the thermodynamic analysis of autothermal dry glycerol reforming for hydrogen production. The study was targeted at identifying the thermodynamic domain of the process operation and variation of the product distribution pattern with process parameters. The thermodynamic analysis using Gibb energy minimization method revealed that the hydrogen production increases with increase in temperature. Whereas, the increase in the CO_2 to glycerol ratio and O_2 to glycerol ratio decreases the hydrogen production. However, lower CO_2 to glycerol ratio and O_2 to glycerol ratio were found to reduce carbon formation. The optimum thermoneutral condition for the dry autothermal glycerol reforming reaction was reported at 653.31 °C, 1 atm, O_2 to glycerol ratio of 0.3 and CO_2 to glycerol ratio of 1.

The thermodynamic analysis of autothermal glycerol reforming using Gibbs free minimization energy in a membrane reactor with onsite hydrogen separation has been reported by Wang et al. [34]. The authors considered the effects of reaction temperatures and O_2 to glycerol ratios under the influence of hydrogen separation fractions. The analysis revealed that hydrogen production was significantly influenced by an increase in the reaction temperature. Moreover, the O_2 to glycerol ratio was found to have a greater effect on the hydrogen yield at a high hydrogen removal fraction. The increase in the hydrogen yield as a result of high hydrogen removal was found to induce carbon formation which reduces with increase in the O_2 to glycerol ratio.

Silva et al. [35] studied the thermodynamic analysis of glycerol steam reforming for hydrogen production using Gibbs free energy minimization method in different types of reactors. The thermodynamic analysis was performed considering the effect of removing CO_2 and H_2 in situ as well as the effect of temperature (327—527 °C), water-to-glycerol feed ratio (3—9), pressure (1—5atm), and the fraction of H_2 and CO_2 removal (0—0.99) in conventional, sorption enhanced, membrane and sorption-enhanced membrane reactor. Based on the analysis, maximum hydrogen yield was obtained in the sorption-enhance membrane reactor at 427 °C, and water to glycerol ratio of 9, 1 atm with 0.99 and 0.88 removals of CO_2 and H_2 respectively. While the least hydrogen yield was obtained from the steam glycerol reforming using the conventional reactor. The study also revealed that carbon formation was observed at a water-to-glycerol ratio of 3. The study inferred that higher water-to-glycerol ratio and lower pressure promotes high hydrogen yield in steam glycerol reforming using sorption enhanced membrane reactor. Since temperature for steam glycerol reforming is limited to the range of 327—527 °C, it will be necessary to further explore the

thermodynamic behavior of the steam glycerol reforming reaction at temperature >527 °C in sorption enhanced membrane reactor to determine its effects on the hydrogen production.

Seretis and Tsiakaras [31] investigated the thermodynamic analysis of aqueous phase glycerol reforming for hydrogen production using the Gibbs free energy minimization method. The authors examined the effect of water to glycerol ratio (4—14), total pressure to saturated vapour pressure ratio (1—2), temperature (27—277 °C) on hydrogen production and carbon formation. The findings show that high hydrogen selectivity of 70% was attained at high temperature and low pressure but with the influence of side reaction such as methanation. In addition, the study shows that carbon formation can be eliminated when the ratio of total pressure to the saturated vapour pressure is less than 1.4 and the temperature greater than 127 °C.

Kinetic studies of hydrogen production by thermo-chemical conversion of glycerol and glycerol conversion pathway

Hydrogen production via thermo-catalytic conversion of glycerol involves several complex networks of catalyzed reactions [36]. The design, synthesis and optimization of the catalytic performance in such complex reactions in a major focal point for researchers. Kinetic analyses and mechanistic studies are key to achieving the proper design of catalysts that can perform at optimum conditions in these complex chemical reactions. Several studies have been reported on the kinetics of glycerol reforming reactions over different types of catalysts (Table 1).

The kinetics of hydrogen production by autothermal glycerol reforming of crude glycerol over promoted 5% Ni/CeZr catalysts was studied by Ghani et al. [37]. The kinetics analysis was performed at a temperature ranged of 500—600 °C, steam-to-carbon ratio of 1.6—3.6, oxygen-to-carbon ratio of 0.05—0.2 and weight hourly space velocity of 0—158.2 g_{cat} min/mol. The variation of the catalyst particle size and the inlet flow rates revealed that the kinetic runs were devoid of heat and mass transfer limitation. The analysis of the kinetic data using power-law model resulted in activation energy of 93.7 kJ/mol with reaction orders of 1, 0.5, and 2 for the glycerol, steam and O_2, respectively. In a similar study, Adhikari et al. [38] reported the kinetics analysis of glycerol steam reforming over Ni/CeO_2 catalyst using power-law model. The analyses of the kinetic data which was obtained at a temperature range of 600—750 °C gave activation energy of 103.4 kJ/mol and reaction order of 0.233. It is obvious that the nature of the catalytic material plays a significant role in breaking the energy barrier during the pyrolysis reaction which explains the difference in the activation energy obtained using Ni/CeO_2 catalyst and promoted 5% Ni/CeZr catalysts. Also, in the work of Dave et al. [39] who employed 15% Ni—10% ZrO_2/CeO_2 as a catalyst in the glycerol steam reforming reaction to produce hydrogen at a temperature range of 600—700 °C, activation energy of 43.4 kJ/mol was obtained using power law. Although, the power-law rate model has been widely used for kinetic modeling in reaction engineering with some degree of predictive accuracy.

Table 1 – Selected literature on the kinetic studies of hydrogen production by thermo-catalytic conversion of glycerol.

Catalysts	Synthesis method	Glycerol conversion method	Reaction conditions	Kinetic models	Activation energy (kJ/mol)	Reference
Ni/SBA-15	Hydrothermal	Glycerol pyrolysis	1 atm, 30–600 °C	Ozawa-Flynn-Wall and Kissinger-Akahira-Sunise	107.3	[43]
3%Pr-Ni/α-Al$_2$O$_3$ catalyst	Wet impregnation	Glycerol pyrolysis	1 atm, 700–800 °C	Langmuir-Hinshelwood and Power law	7.14 kJ/mol, and 37.36	[40]
5% Ni/CeZr	Wet impregnation	Glycerol autothermal	1 atm, 500–600 °C	Power-law	93.7	[37]
Ni/CeO$_2$	Incipient wet impregnation	Glycerol steam reforming	1 atm, 600–750 °C	Power law	103.4	[38]
15% Ni–10% ZrO$_2$/CeO$_2$	Wet impregnation	Glycerol steam reforming	1 atm, 600–700 °C	Power-law	43.4	[39]
15% Ni/CeO$_2$	Deposition precipitation	Glycerol steam reforming	1 atm, 400–700 °C	Langmuir-Hinshelwood	35.6	[47]
15% Co/Al$_2$O$_3$	Wet impregnation	Glycerol steam reforming	1 atm, 450–550 °C	Power-law	67.2	[128]
5% Co–10% Ni/Al$_2$O$_3$	Co-impregnation	Glycerol steam reforming	1 atm, 500–550 °C	Langmuir-Hinshelwood and Eley-Rideal kinetic models	63.3	[129]

However, the detail mechanistic steps involved in the complex reaction cannot be explained using the power-law model. Proper understanding of a gas-phase reaction and designing of a suitable catalytic system for such reaction requires a comprehensive knowledge of the reaction pathways.

In order to determine the detail mechanistic study of glycerol conversion to hydrogen, Shihirah et al. [40] reported the kinetics and mechanisms of hydrogen production by pyrolysis of glycerol over 3%Pr-Ni/α-Al$_2$O$_3$ catalyst. The kinetic data were measured at a temperature range of 700–800 °C and analyzed using power-law, and Langmuir-Hinshelwood kinetic models. The analysis of the kinetic data resulted in activated energy of 7.14 kJ/mol, and 37.36 kJ/mol for the power-law and the Langmuir-Hinshelwood models, respectively. The mechanistic study of the glycerol pyrolysis revealed that the single site associative adsorption with molecular surface reaction was the rate-determining steps for the pyrolysis of glycerol over 3%Pr-Ni/α-Al$_2$O$_3$ catalyst. In a similar study by Cheng et al. [41,42], 15% Co/Al$_2$O$_3$ and 5% Co–10% Ni/Al$_2$O$_3$ were used as catalysts in glycerol steam reforming for hydrogen production at a temperature range of 450–550 °C. The kinetic data obtained in the glycerol steam reforming over the 15% Co/Al$_2$O$_3$ was analyzed using power-law and the activation energy estimated as 67.2 kJ/mol. Whereas, the kinetic data obtained in the glycerol steam reforming over the 5% Co–10% Ni/Al$_2$O$_3$ was analyzed using the Langmuir-Hinshelwood model and the activation energy estimated as 63.3 kJ/mol. Certainly, the kinetics analysis of any glycerol conversion process is to a large extent dependent on the composition of the catalysts.

Besides glycerol conversion by reforming, the kinetic studies of hydrogen production by glycerol pyrolysis has been investigated by Oliveiramaia et al. [43] at a temperature range of 30–600 °C using a thermogravimetric analyzer. The analysis of the kinetic data was based on the methods of Ozawa-Flynn-Wall and Kissinger-Akahira-Sunise to obtain activation energy of 107.03 kJ/mol for both methods. Also, Panagiotopoulou et al. [44] in their studies on the kinetics and mechanisms of glycerol photo-oxidation and photo-reforming reaction over TiO$_2$ and Pt/TiO$_2$ photocatalysts observed that a very slow reaction was obtained over TiO$_2$ compared to a rapid and efficient reaction over the Pt/TiO$_2$ photocatalyst. The study revealed that both the glycerol photo-oxidation and photo-reforming gave the same reaction intermediates which imply that the overall reaction pathways in both the glycerol photo-oxidation and photo-reforming were the same. The main mechanism for hydrogen production during the photo-reforming was found to be the reduction of water to H$_2$ via photogenerated electrons. In a separate study, the mechanism for catalyzed glycerol pyrolysis has been proposed by Ng et al. [45] (Fig. 3). In a typically catalyzed glycerol pyrolysis, there is formation of unreacted residues that can further be converted into intermediate products. At a very high pyrolysis temperature and enough residence time, the formation of gaseous products is favoured. Otherwise, the pyrolysis reaction favours the formation of bio-oils. The glycerol pyrolysis in the presence of catalysts increases hydrogen selectivity and yield unlike the uncatalyzed reaction which favours high selectivity of CO$_2$.

The pathway for the conversion of glycerol to gaseous products is depicted in Fig. 4 where (1)–(4) represent the
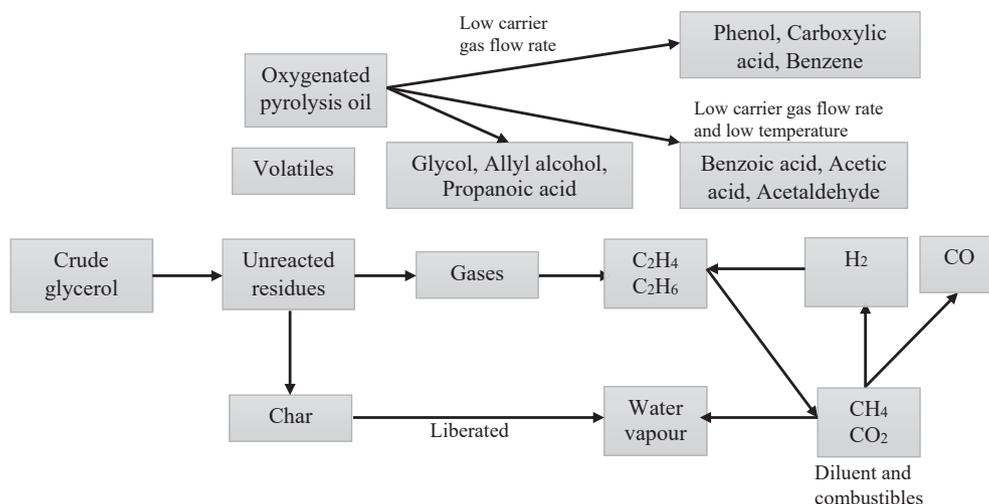
Fig. 3 — Proposed mechanism for carbonaceous catalyst-assisted microwave-heated crude glycerol pyrolysis (Ng et al. [45]).

sequence of the reaction. Based on the experimental report by Nabgan et al. [46], during steam reforming process, adsorbed glycerol is dehydrogenated to C_3H_xO intermediates on the active site of the supported metal-based catalysts. An adsorbed CH_yO is formed from the C-C bonds of the adsorbed intermediates which are subsequently dehydrogenated to for adsorbed CO. In the course of the steam reforming reactions, the adsorbed CO were liberated to gaseous CO via water gas shift reaction. The overall glycerol steam reforming reaction comes with the evolution of hydrogen and CO gases.
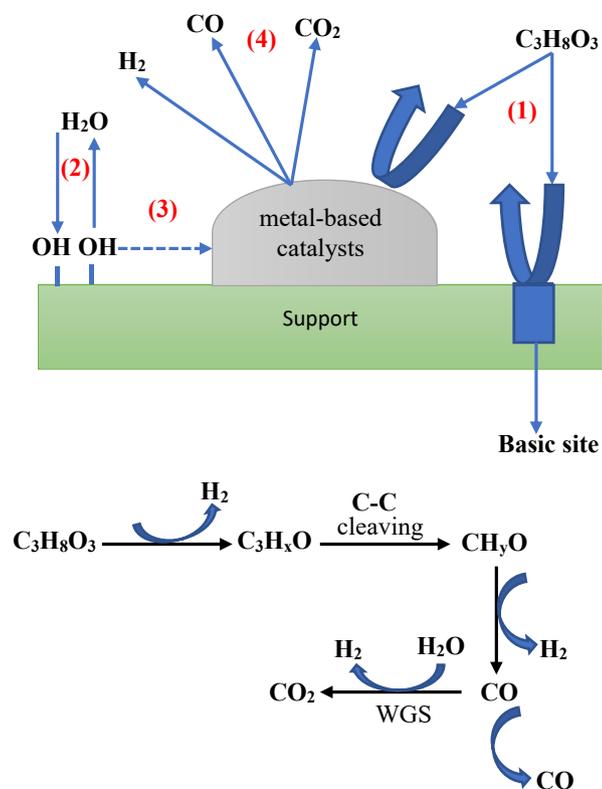

Fig. 4 — Glycerol conversion pathway to gaseous products by steam reforming process [46]).

Overview of thermo-catalytic routes for hydrogen production from glycerol

Steam reforming of glycerol

Steam reforming is a well-known technique used presently in the chemical industry for the production of hydrogen and syngas from natural gas [48–50]. In this technique, steam at high temperature and pressure are utilized for the reforming process in the presence of a catalyst [51–53]. There is an increasing research interest in the development of a small-scale steam reforming process that could supply hydrogen for fuel cells application using feedstocks such as glycerol, methanol, and ethanol [22,54,55]. Steam glycerol reforming is an important technological route for the production of hydrogen from biomass [56–58]. According to Wang et al. [59], the steam glycerol reforming represented in Equation (1) involves the production of 7 moles of hydrogen from 1 mole of glycerol. The occurrence of steam glycerol reforming in Equation (1) in a function of the glycerol decomposition and water gas shift reaction in Equations (2) and (3), respectively [60]. Based on thermodynamic analysis, the steam glycerol reforming reaction requires high temperature, low pressure and high water/glycerol molar ratio for hydrogen production [29,35,61]. Since the glycerol steam reforming occurs at high temperature, the formation of carbon by Bouduard reaction (Equation (4)) is usually induced and this often results in the deactivation of the active site of the catalysts [62].

$$C_3H_{8}O_{3(g)} + 3H_2O_{(g)} \leftrightarrow 3CO_{(g)} + 7H_{2(g)} \tag{1}$$

$$C_3H_{8}O_{3(g)} \leftrightarrow 3CO_{(g)} + 4H_{2(g)} \tag{2}$$

$$CO_{(g)} + 3H_2O_{(g)} \leftrightarrow CO_{(g)} + H_{2(g)} \tag{3}$$

$$2CO \leftrightarrow C_{(g)} + CO_{2(g)} \tag{4}$$
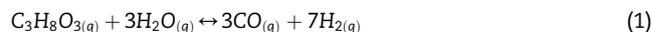
Due to its importance as a feasible means of hydrogen production and the high tendency of adapting the existing technology used in steam reforming of natural gas, there has

been tremendous interest in steam glycerol reforming in the past one decade. Several studies have reported the use of supported metal catalysts for hydrogen production by steam glycerol reforming as shown in Table 2. Based on these studies, several factors such as the composition of the catalyst, the type of support, the use of promoters, the configuration of the reactor, the catalyst synthesis method, the reaction conditions have been found to significantly influence hydrogen production from the steam glycerol reforming.

On the effect of support on catalytic activity, Huang et al. [63] reported that the catalytic performance of 10%Ni/Al$_2$O$_3$ catalyst in steam glycerol reforming reaction was significantly enhanced when the Al$_2$O$_3$ support was modified with CaO-MgO. The unmodified 10%Ni/Al$_2$O$_3$ catalysts tested in the steam glycerol reforming reaction at 800 °C using water to glycerol ratio of 3 resulted in hydrogen yield of 51.68% which is lower compared to 88.43% obtained using the CaO-MgO modified 10%Ni/Al$_2$O$_3$ catalyst. This suggests that the CaO-MgO being basic oxides helped in suppressing the deactivation of the catalytic via Boudouard reaction. This was confirmed from the analysis of the used catalyst for carbon deposition. The used 10%Ni/Al$_2$O$_3$ catalyst was found to contain 43.21% of carbon compared to the used CaO-MgO modified 10%Ni/Al$_2$O$_3$ with 10.78% of carbon deposition.

Considering the effect of supports on noble metal catalysts such as Pt for glycerol steam reforming, Sad et al. [64] reported the activity of Pt catalyst synthesized on different supports during steam glycerol reforming. The Pt was synthesized on SiO$_2$, MgO, Al$_2$O$_3$ and TiO$_2$ using incipient wet impregnation method and tested in steam glycerol reforming for hydrogen production at 350 °C using 10% wt. glycerol. The findings show that the activity of the Pt in the steam glycerol reforming reaction was influenced by the nature of the support materials. Hydrogen yield of 60.00%, 59.00%, 62.00% and 62.00% were reported for the Pt/SiO$_2$, Pt/MgO, Pt/Al$_2$O$_3$, and Pt/TiO$_2$, respectively. The varying catalytic performance can be attributed to the extent of interaction between the Pt and the various support which is in conformity with the work of Zhang et al. [65]. As reported by Zhou et al. [66], the interaction between Pt and the various support involved electron transfer from the Pt to the support and the spillover of oxygen from the support to the Pt at the Pt-support interface. It is well established in the literature that the redox properties of supported Pt catalysts are to a large extent determined by the Pt-support interaction [65–67]. Usually, a good support material enhances metal dispersion during synthesis thereby increasing the metal surface area for the catalytic reaction [68,69]. Interestingly, all the catalysts displayed nearly 100% glycerol conversion during the steam glycerol reforming reaction. The characterization of the used catalysts shows that the Pt/SiO$_2$ and Pt/MgO catalysts with 6.2 and 8.4 μmol carbon deposited per 1 m^2 of the catalyst, respectively were more stable than the Pt/Al$_2$O$_3$, and Pt/TiO$_2$ catalysts with 49.5 and 29.8 μmol carbon deposited per 1 m^2 of the catalyst, respectively. One major factor that could be responsible for this variation in the stability of the catalysts is the basicity of the support material which is consistent with the work of García-Vargas et al. [70] who confirmed that high catalyst basicity helps minimize carbon formation and deposition.

Also using a noble metal catalyst, Kousi et al. [58] investigated the effect of modification on the catalytic activity of 5% Ru/γ-Al$_2$O$_3$ in steam glycerol reforming to hydrogen. The 5% Ru/γ-Al$_2$O$_3$, 5%Ru/B$_2$O$_3$-Al$_2$O$_3$, 5%Ru/MgO-Al$_2$O$_3$ catalysts were synthesized using wet co-impregnation method and tested in steam glycerol reforming reaction for hydrogen production at 600 °C using 20:80 wt% glycerol/water solution. The findings revealed that the catalytic activity of the Ru-catalysts was strongly dependent on the nature of the support [71]. Hydrogen yield of 68.00%, 67.00%, and 37.00% was obtained for the 5%Ru/γ-Al$_2$O$_3$, 5%Ru/B$_2$O$_3$- Al$_2$O$_3$, 5%Ru/MgO-Al$_2$O$_3$ catalysts, respectively which implies that the modification did not improve the catalytic activity of the 5%Ru/γ-Al$_2$O$_3$ unlike that reported by Sad et al. [64] for Pt-catalysts. Similarly, the effect of synthesizing different noble metals on the same support was investigated for steam glycerol reforming to hydrogen by Senseni et al. [72]. The Pt/MgAl$_2$O$_4$, Ru/MgAl$_2$O$_4$, Ir/MgAl$_2$O$_4$, and Rh/MgAl$_2$O$_4$ synthesized by wet impregnation and tested in steam glycerol reforming to hydrogen at 600 °C using water to glycerol molar ratio of 9 to 1 resulted in the hydrogen yield of 93.00%, 94.00%, 96.00%, and 98.00%, respectively. It can be seen that the Rh/MgAl$_2$O$_4$ displayed superior catalytic activity in terms of the product yield compared to the other MgAl$_2$O$_4$ supported noble metal catalyst. This was attributed to its outstanding physicochemical properties compared to other catalysts.

Besides the influence of supports, studies have shown that the use of promoters can also enhance catalytic performance during steam glycerol reforming. In line with this, the work of Charisiou et al. [73] revealed that the performance of 10%Ni/ CaO-MgO-Al$_2$O$_3$ catalyst was significantly improved by the addition of La, Ce, Zr promoters. The promoted catalyst was found to show excellent activity and stability with hydrogen yield and glycerol conversion of 54.53% and 98.72%, respectively. The carbon analysis of the used promoted catalyst revealed that only 0.67% of carbon was deposited in the catalyst after 18 h time-on-stream of the steam glycerol reforming reaction.

Also, appropriate catalyst design using the combination of different metal catalysts have been shown to significantly affect hydrogen production by steam glycerol reforming [74,75]. Wang et al. [59] investigated the catalytic activity of Ni-Cu-Al, Ni-Cu-Mg, and Ni-Cu prepared by co-precipitation in steam glycerol reforming to hydrogen at 650 °C under atmospheric pressure. The results show that the hydrogen yield obtained from the steam glycerol reforming was dependent on the nature of the catalyst used. Hydrogen yield of 92.00%, 28.00% and 62.00% was obtained for Ni-Cu-Al, Ni-Cu-Mg, and Ni-Cu, respectively. The results revealed that there is a synergistic interaction between Ni, Cu and Al culminating to an excellent catalytic performance. The catalytic performance can also be linked to the catalyst physicochemical properties such as the BET specific surface area. It can be seen that catalytic activity of the Ni-Cu-Al, Ni-Cu-Mg, and Ni-Cu correspond to the BET specific surface area, which was estimated as 34.8, 15.62, and 33.56 m^2/g, respectively.

Furthermore, the use of perovskite-type catalysts such as LaNiO$_3$ and LaCoO$_3$ have been reported by Aman et a [76]. for steam glycerol reforming to hydrogen. The perovskite LaNiO$_3$ and LaCoO$_3$ catalysts were prepared by a reverse

Table 2 – Summary of selected literature on hydrogen production by steam glycerol reforming.

Catalyst	Preparation method	Type of reactor	S_{BET} (m²/g)	Reaction conditions	Feed composition	Glycerol conversion	Hydrogen yield	H₂/CO ratio	Reference
10%Ni/Al₂O₃	Incipient wet impregnation	Fixed bed reactor	n.r	800 °C/1 bar, GHSV = 5000h-1, TOS:	H₂O: glycerol molar ratio: 3:1	81.43%	50.98%	2.1	[63]
10%Ni/CaO-MgO-Al₂O₃	Incipient wet impregnation	Fixed bed reactor	n.r	800 °C/1 bar, GHSV = 5000h-1, TOS:	H₂O: glycerol molar ratio: 3:1	88.43%	51.68%	2.0	[63]
10%NiLaCeZr/CaO-MgO- Al₂O₃	Incipient wet impregnation	Fixed bed reactor	n.r	800 °C/1 bar, GHSV = 5000h-1, TOS:	H₂O: glycerol molar ratio: 3:1	98.72%	54.53%	2.3	[73]
LaNiO₃	reverse microemulsion	Fixed bed reactor	75.7	700 °C/1 bar, TOS:	H₂O: glycerol molar ratio: 9:1	99.80%	90.00%	N.R	[76]
LaCoO₃	reverse microemulsion	Fixed bed reactor	25.6	700 °C/1 bar, TOS:	H₂O: glycerol molar ratio: 9:1	92.00%	50.00%	N.R	[76]
Rh/Al₂O₃	n.r	Fixed bed reactor	n.r	400 °C/4.5 bar, TOS:	H₂O: glycerol molar ratio: 19:1	72.00%	2.6 mol/glycerol	5.7	[58]
Pt/MgAl₂O₄	wet-impregnation	Fixed bed reactor	85.56	600°/1 bar, GHSV = 35,000 mL g⁻¹ h⁻¹, TOS:	H₂O: glycerol molar ratio: 9:1	96.00%	93.00%	N.R	[72]
Ru/MgAl₂O4	wet-impregnation	Fixed bed reactor	159	600°/1 bar, GHSV = 35,000 mL g⁻¹ h⁻¹, TOS:	H₂O: glycerol molar ratio: 9:1	91.00%	94.00%	N.R	[72]
Ir/MgAl₂O4	wet-impregnation	Fixed bed reactor	120.84	600°/1 bar, GHSV = 35,000 mL g⁻¹ h⁻¹, TOS:	H₂O: glycerol molar ratio: 9:1	90.00%	96.00%	N.R	[72]
Rh/MgAl₂O₇	wet-impregnation	Fixed bed reactor	95.33	600°/1 bar, GHSV = 35,000 mL g⁻¹ h⁻¹, TOS:	H₂O: glycerol molar ratio: 9:1	98.00%	98.00%	8.9	[72]
5%Ni/Al₂O₃	Sol-gel	Fixed bed reactor	183.5	750°/1 bar, GHSV = 35,000 mL g⁻¹ h⁻¹, TOS:	H₂O: glycerol molar ratio: 9:1	95.00%	98.75%	n.r	[60]
10%Ni/Al₂O₃	Sol-gel	Fixed bed reactor	176.6	750°/1 bar, GHSV = 35,000 mL g⁻¹ h⁻¹, TOS:	H₂O: glycerol molar ratio: 9:1	97.00%	99.20%	n.r	[60]
15%Ni/Al₂O₃	Sol-gel	Fixed bed reactor	158.3	750°/1 bar, GHSV = 35,000 mL g⁻¹ h⁻¹, TOS:	H₂O: glycerol molar ratio: 9:1	98.00%	99.80%	9.8	[60]
20%Ni/Al₂O₃	Sol-gel	Fixed bed reactor	143.3	750°/1 bar, GHSV = 35,000 mL g⁻¹ h⁻¹, TOS:	H₂O: glycerol molar ratio: 9:1	96.00%	99.60%	n.r	[60]
Ni-Cu-Al	Co-precipitation	Fixed bed reactor	34.82	650°/1 bar, GHSV: nr, TOS:	n.r	92.00%	92.00%	8.9	[59]
Ni-Cu-Mg	Co-precipitation	Fixed bed reactor	15.62	650°/1 bar, GHSV = n.r, TOS:	n.r	48.00%	28.00%	4.8	[59]
Ni-Cu	Co-precipitation	Fixed bed reactor	33.56	650°/1 bar, GHSV = n.r, TOS:	n.r	78.00%	62.00%	7.2	[59]
Pt/SiO₂	Incipient wet impregnation	Fixed bed reactor	230	350°/1 bar, GHSV = n.r, TOS:	10% wt. glycerol	100.00%	60.00%	2.7	[64]
Pt/MgO	Incipient wet impregnation	Fixed bed reactor	180	350°/1 bar, GHSV = n.r, TOS:	10% wt. glycerol	100.00%	59.00%	2.7	[64]
Pt/Al₂O₃	Incipient wet impregnation	Fixed bed reactor	186	350°/1 bar, GHSV = n.r, TOS:	10% wt. glycerol	100.00%	62.00%	2.6	[64]
Pt/TiO₂	Incipient wet impregnation	Fixed bed reactor	106	350°/1 bar, GHSV = n.r, TOS:	10% wt. glycerol	95.00%	62.00%	3.1	[64]
5%Ru/γ-Al₂O₃	wet-co-impregnation	Fixed bed plug reactor	185	600 °C/1 bar, GHSV = n.r, TOS:	20:80 wt% glycerol/water solution	92.00%	68.00%	0.9	[58]
5%Ru/B₂O₃- Al₂O₃	wet-co-impregnation	Fixed bed plug reactor	188	600 °C/1 bar, GHSV = n.r, TOS:	20:80 wt% glycerol/water solution	82.00%	67.00%	1.0	[58]
5%Ru/MgO-Al₂O₃	wet-co-impregnation	Fixed bed plug reactor	108	600 °C/1 bar, GHSV = n.r, TOS:	20:80 wt% glycerol/water solution	52.00%	37.00%	0.9	[58]

n.r: not reported.

microemulsion method and employed in steam glycerol reforming reaction at 700 °C using water to glycerol molar ratio of 9 to 1. The finding shows that the LaNiO$_3$ catalyst with hydrogen yield of 90.00% displayed a superior activity compared to the LaCoO$_3$ catalyst with hydrogen yield of 50.00%. Excellent performance of the perovskite LaNiO$_3$ could be attributed to the presence of the Ni-active site which has a high affinity for hydrogen production compared to Co species. However, the LaCoO$_3$ catalyst was found to be more resistant to carbon deposition compared to the LaNiO$_3$ catalyst. Based on the characterization of the used catalysts, 0.054 g of carbon was found to be deposited on the LaNiO$_3$ catalyst compared to 0.004 g of carbon found to be deposited on the LaCoO$_3$ catalyst per hour. Generally, cobalt-based catalyst has been reported to have better stability compared to Ni-based catalysts [77,78].

Variation of metal loading during catalyst synthesis has been reported to also have a significant effect on catalytic activity [79,80]. Senseni et al. [60] revealed that the variation of Ni-loading significantly influence the activity of Al$_2$O$_3$ supported Ni catalyst during steam glycerol reforming. The catalytic activities of the 5%Ni/Al$_2$O$_3$, 10%Ni/Al$_2$O$_3$, 15%Ni/Al$_2$O$_3$, and 20% Ni/Al$_2$O$_3$ catalysts in the steam glycerol reforming at 750 °C resulted in hydrogen yield of 98.75%, 99.20%, 99.80%, and 99.60%, respectively. It is obvious that the activity of the Ni/Al$_2$O$_3$ catalyst increases until 15% Ni-loading and thereafter dropped. The decline in the catalytic activity at high Ni-loading could be attributed to sintering effect on the catalyst active site [81].

The utilization of each of the catalysts summarized in Table 2 in the steam glycerol reforming resulted in syngas ratios ranges from 0.9 to 9.8. Syngas is one of the key feedstocks for the production of methanol which can serve as alternative fuel or subsequently used as chemical intermediates for the production of other valuable chemicals [82]. Moreover, syngas with H$_2$: CO ratio close to unity can be employed for the production of synthetic fuel through Fischer-Tropsch synthesis [83]. Interestingly, hydrogen can be produced from syngas via water gas shift reaction over iron oxide catalysts at 300−500 °C [84]. The focal point in the production of hydrogen by steam glycerol reforming remain the design and development of effective catalysts with high activity and stability. There is no consensus in the literature as per the most effective method for synthesis of catalysts that are highly active and stable in steam glycerol reforming. Hence, these call for more intensive research in employing advanced synthesis techniques that can be employed for more effective catalysts for hydrogen production by steam glycerol reforming. Furthermore, research efforts should be geared toward discovering suitable reaction conditions that can facilitate the optimum performance of the catalysts. These can be achieved using appropriate design of experiment and optimization techniques.

Dry reforming of glycerol

The dry reforming reaction involves the utilization of CO$_2$ as an oxidant for catalytic conversion of hydrocarbon (e.g. natural gas) or biomass (e.g. glycerol) to hydrogen, syngas and other gaseous products [85,86]. Although, the reaction was first investigated in a laboratory-scale by Fisher and Tropsh in 1928 over Ni and Co catalysts, however, there was no much awareness until the last three decades [87,88]. The interest in dry reforming reaction was stimulated by the adverse effect of CO$_2$ emission on the environment viz. global warming [89,90]. Hence, research efforts have focused on the sustainable utilization of CO$_2$ for the production of value-added chemicals [91−94]. The utilization of CO$_2$ as an oxidant for the reforming of glycerol is a relatively new area of research in gas-phase reaction engineering. The awareness of the importance of dry reforming of glycerol started in 2004 and has witnessed a progressive trend until 2018. The growing interest in the dry reforming of glycerol could be attributed to its potential as a technical route for CO$_2$ mitigation, conversion of glycerol, a by-product of biodiesel and the production of hydrogen and syngas suitable for use as feedstocks in Fischer-Tropsch synthesis (FTS) and Methanol-to-gas (MTG) processes for production of olefins, alkane and other valuable chemicals [95]. The main chemical reactions involved in dry reforming of glycerol are represented by Equations (5) with competing reactions such as decomposition of glycerol (Equation (6)), water gas shift reaction (Equation (7), methanation (Equations (8−10)) and deposition and carbon gasification reaction (Equations (11−14)) [96].

Glycerol reforming reaction

$$C_3H_8O_3 + CO_2 \leftrightarrow 4CO + 3H_2 + H_2O \qquad (5)$$
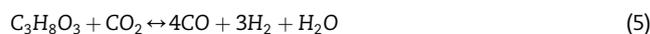
Competing reaction
Decomposition of glycerol

$$C_3H_8O_3 \leftrightarrow 3CO + 4H_2 \qquad (6)$$

water-gas shift reaction

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad (7)$$

Methanation

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad (8)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad (9)$$

$$3H_2 + 2CO \leftrightarrow CH_4 + CO_2 \qquad (10)$$

Deposition and gasification of carbon

$$2CO \leftrightarrow C + CO_2 \qquad (11)$$

$$CH_4 \leftrightarrow C + 2H_2 \qquad (12)$$

$$C + H_2O \leftrightarrow H_2 + CO \qquad (13)$$

$$C + 2H_2O \leftrightarrow 2H_2 + CO_2 \qquad (14)$$

In the past decade, several studies have been reported on the use of supported metal catalysts for dry reforming of glycerol to hydrogen as summarized in Table 3. The different reported studies considered the effects of metal loading, nature of support, the effect of promoters, the reaction conditions, and the synthesis methods on the catalytic activity in terms of hydrogen production and glycerol conversion.

Arif et al. [95] investigated the promotional effect of Re on the catalytic performance of Ni/CaO catalyst in dry reforming

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Table 3 — Summary of selected literature on hydrogen production by dry reforming of glycerol.

Catalysts	Synthesis method	S_{BET} (m^2/g)	Reactor Type	Reaction condition	Glycerol conversion (%)	H_2 yield (%)	H_2/CO ratio	References
3% La-20%Ni/Al$_2$O$_3$	Wet-impregnation	96.00	Fixed bed reactor	850 °C/1 bar, CO$_2$: glycerol ratio = 1.67, WHSV = 3.6 × 10^4 ml g^{-1} S^{-1}, TOS:	98.00	97.25	0.8	[101]
15% Ni/CaO	Wet-impregnation	42.98	Fixed bed reactor	900 °C/1 bar, CO$_2$: glycerol ratio = 1.67, GHSV = 3.6 × 10^4 ml g$_{cat}$ S^{-1}, TOS:	35.00	30.00	n.r	[95]
5% Re-15%Ni/CaO	Wet-impregnation	26.64	Fixed bed reactor	900 °C/1 bar, CO$_2$: glycerol ratio = 1.67, GHSV = 3.6 × 10^4 ml g$_{cat}$ S^{-1}, TOS:	61.00	56.00	0.8	[95]
5%Ni/Cement clicker	Wet-Co-impregnation	7.73	Fixed bed reactor	750 °C/1 bar, CO$_2$: glycerol ratio = 1 GHSV = 3.6 × 10^4 ml g$_{cat}$ S^{-1}, TOS:	53.40	28.60	0.4	[99]
10%Ni/Cement clicker	Wet-Co-impregnation	15.81	Fixed bed reactor	750 °C/1 bar, CO$_2$: glycerol ratio = 1 GHSV = 3.6 × 10^4 ml gcat S^{-1}, TOS:	46.10	24.20	0.4	[99]
15%Ni/Cement clicker	Wet-Co-impregnation	17.30	Fixed bed reactor	750 °C/1 bar, CO$_2$: glycerol ratio = 1, GHSV = 3.6 × 10^4 ml gcat S^{-1}, TOS:	63.80	50.40	1.1	[99]
20%Ni/Cement clicker	Wet-Co-impregnation	17.83	Fixed bed reactor	750 °C/1 bar, CO$_2$: glycerol ratio = 1 GHSV = 3.6 × 10^4 ml gcat S^{-1}, TOS:	75.60	69.30	1.1	[99]
15%Ni/Al$_2$O$_3$	Wet impregnation	6.34	Fixed bed reactor	700 °C/1 bar, CO$_2$: glycerol ratio = 1 GHSV = 3.6 × 10^4 ml g$_{cat}$ S^{-1}, TOS:	13.07	10.18	0.7	[19]
1%Ag -15%Ni/Al$_2$O$_3$	Wet impregnation	2.43	Fixed bed reactor	700 °C/1 bar, CO2: glycerol ratio = 1 GHSV = 3.6 × 10^4 ml gcat S^{-1}, TOS:	23.93	21.49	0.6	[19]
3%Ag -15%Ni/Al$_2$O$_3$	Wet impregnation	2.43	Fixed bed reactor	700 °C/1 bar, CO$_2$: glycerol ratio = 1 GHSV = 3.6 × 10^4 ml gcat S^{-1}, TOS:	33.41	26.29	0.4	[19]
5%Ag -15%Ni/Al$_2$O$_3$	Wet impregnation	1.18	Fixed bed reactor	700 °C/1 bar, CO$_2$: glycerol ratio = 1, TOS: WHSV = 36 L gcat^{-1} h^{-1}, TOS:	32.97	24.36	0.4	[19]
5%Ni/Al$_2$O$_3$	Sol-gel	183.00	Fixed bed reactor	750 °C/1 bar, CO$_2$: glycerol ratio = 1, GHSV: 1.5 × 10^4 ml g^{-1} h^{-1}, TOS:	88.00	70.00	0.7	[96]
10%Ni/Al$_2$O$_3$	Sol-gel	177.00	Fixed bed reactor	750 °C/1 bar, CO$_2$: glycerol ratio = 1, GHSV: 1.5 × 10^4 ml g^{-1} h^{-1}, TOS:	94.00	82.00	0.7	[96]
15%Ni/Al$_2$O$_3$	Sol-gel	158.00	Fixed bed reactor	750 °C/1 bar, CO$_2$: glycerol ratio = 1, GHSV: 1.5 × 10^4 ml g^{-1} h^{-1}, TOS:	96.00	84.00	0.8	[96]
20%Ni/Al$_2$O$_3$	Sol-gel	143.00	Fixed bed reactor	750 °C/1 bar, CO$_2$: glycerol ratio = 1, GHSV: 1.5 × 10^4 ml g^{-1} h^{-1}, TOS:	93.00	83.00	0.7	[96]
1%Rh/CeO$_2$	Wet impregnation	10.20	Packed bed reactor	750 °C/1 bar, CO$_2$: glycerol ratio = 1, TOS:	72.00	21.30	1.1	[102]
1%Rh/ZrO$_2$	Wet impregnation	16.30	Packed bed reactor	750 °C/1 bar, CO$_2$: glycerol ratio = 2, TOS:	78.00	24.20	1.1	[102]

n.r: not reported.

of glycerol. Both the unpromoted 15% Ni/CaO and 5% Re-promoter-15%Ni/CaO prepared by co-precipitation were tested in dry reforming of glycerol at 900 °C using CO_2 to glycerol ratio of 1.67 and gas hourly space velocity of 3.6×10^4 ml $g_{cat} S^{-1}$. The glycerol steam reforming reaction over the 5% Re-promoter-15%Ni/CaO catalyst resulted in hydrogen yield and glycerol conversion of 56% and 61.00%, respectively which is higher compared to using the unpromoted 15% Ni/CaO catalyst with hydrogen yield and glycerol conversion of 30.00% and 35.00%, respectively. It is evident that the addition of the Re-promoter enhanced the catalytic performance of the Ni/CaO catalyst. Studies have shown that the addition of a small amount of noble metals such as Re could help in preventing sintering of Ni-active sites during reforming reaction [97,98]. Moreover, the addition of the Re-promoter also helps in the stability of the Ni/CaO catalysts as evidence in the characterization of the used catalysts. The gasification of the deposited carbon using temperature-programmed oxidation revealed that the used Ni/CaO catalyst has more than 13.27% carbon gasified compared to the Re-promoted Ni/CaO catalyst.

In a similar study by Harun et al. [19], the effect of Ag promoter on the catalytic activity of 15%Ni/Al$_2$O$_3$ in dry reforming of glycerol was reported. The catalytic performance of the Ag promoted Ni/Al$_2$O$_3$ catalyst in dry reforming of glycerol at 700 °C was reported to be more superior than the unpromoted 15%Ni/Al$_2$O$_3$ catalyst. However, the catalytic activity of the Ag promoted 15%Ni/Al$_2$O$_3$ catalysts were found to varies with the Ag loading which ranges from 1-5 wt%. The highest hydrogen yield and glycerol conversion of 26.29% and 33.41%, respectively were obtained using the 3%Ag -15%Ni/ Al$_2$O$_3$ catalyst in the dry reforming of glycerol which is higher compared to the unpromoted 15%Ni/Al$_2$O$_3$ with hydrogen yield and glycerol conversion of 10.18% and 13.07%, respectively. In conformity with the study of Arif et al. [95], it is evident that the Ag promoter improved the catalytic activity of the 15%Ni/Al$_2$O$_3$ catalyst. Also, Ag being a noble metal aid the prevention of the sintering of the Ni-catalyst during the dry reforming of glycerol.

In addition to the effect of promoters on catalytic activity during dry reforming of glycerol, studies have shown that the variation in metal loading can also affect catalytic performance. In line with this, Lee et al. [99] in their study reported that the variation of Ni-loading significantly influence the catalytic activity of cement clicker supported Ni-catalysts. The catalysts synthesized by wet co-impregnation method with a variation of Ni content from 5 to 20 wt% was tested in dry reforming of glycerol reaction at 750 °C using CO_2 to glycerol ratio of 1. It was observed that the activity of the cement clicker supported Ni-catalyst increases with increase in the Ni-loading. The highest hydrogen yield and glycerol conversion of 69.30% and 75.60% were obtained in the dry reforming of glycerol reaction over the 20%wtNi/cement clicker catalyst. Since, it cannot be ascertained from the study that the optimum catalytic activity was reached at 20 wt% Ni loading, it necessary to determine the optimum Ni-loading that can give the best catalytic performance using the same catalytic system and reaction conditions. Also, it should be borne in mind that high Ni-loading often result in sintering which in turn can deactivate the Ni-active site.

Furthermore, the use of different support materials for the synthesis of metal-based catalysts has been reported to also influence the catalytic activity during dry reforming of glycerol. Bulutoglu et al. [99] revealed that Rh synthesized on CeO$_2$ and ZrO$_2$ support by wet impregnation method displayed different catalytic performance during dry reforming of glycerol at 700 °C. The study revealed that both CeO$_2$ and ZrO$_2$ significantly influence the catalytic performance of the Rh-catalysts. Hydrogen yield and glycerol conversion of 24.20% and 78.00%, respectively were obtained using the Rh/ZrO$_2$ catalyst in the dry reforming of glycerol reaction which is higher compared to 21.30% and 72.00%, respectively obtained for the Rh/CeO$_2$ catalyst. The variation in their performance could be attributed to the respective physicochemical properties such as the BET specific surface area. It can be seen that Rh/ZrO$_2$ catalyst with BET specific surface area of 16.3 m^2/g displayed a higher activity compared to 1%Rh/CeO$_2$ catalyst wit BET specific surface area of 10.2 m^2/g.

Besides having a good prospect as a technological route for the production of hydrogen, the dry glycerol reforming is also a means of producing syngas with ratio suitable as chemical intermediates for the production of synthetic fuel via Fischer-Tropsch synthesis. As summarized in Table 1, the syngas produced from dry glycerol reforming over the different catalyst ranges from 0.4 to 1.1. The obtained H$_2$: CO ratios make the syngas suitable as a good feedstock for the production of synthetic fuel over iron-based catalyst in the Fischer-Tropsch synthesis. It is worthy of note that the syngas ratios obtained from the dry reforming of glycerol vary with the composition of the catalysts. The syngas ratio obtained over most of the noble metals-based catalysts were close to unity.

Although dry reforming of glycerol has several advantages as a technical route for hydrogen production, the process is, however, constraint with challenges such as catalytic deactivation and high thermal energy required for the reaction [100]. The catalyst deactivation often occurs as a result of carbon formation formed during competing reactions such as methane decomposition and Bouduoard reaction. According to Abatzoglou et al. [100] three types of carbons namely encapsulated film, whisky-like, and pyrolytic carbon usually occur at temperature <500 °C, > 450 °C, and >600 °C, respectively. These carbons when deposited on the catalysts surface, tends to cause progressive deactivation and encapsulation of the catalysts active sites resulting in the breakdown of the catalyst structure. Research efforts are now geared towards developing catalytic system with high activity and stability during the dry glycerol reforming reaction.

Partial oxidation reforming of glycerol

Hydrogen production by partial oxidation glycerol reforming entails the thermo-catalytic conversion of glycerol using the sub-stoichiometric amount of oxygen as the oxidant [103]. In comparison with other reforming process using steam and CO_2, the partial oxidation glycerol reforming when operated under atmospheric pressure is self-sustaining [104]. Since the partial oxidation glycerol reforming is an exothermic process, it has the advantages of energy-saving compared with the steam glycerol reforming where high thermal energy is required for steam production and to initiate the reaction. Moreover, the partial oxidation glycerol reforming provides an

opportunity for on-site glycerol abatement which can be incorporated into recycled biodiesel plant structural design [105].

The pioneering work on partial oxidation glycerol reforming was reported by Dauenhauer et al. [104] using ceria modified Al_2O_3 supported Rh catalyst. The catalyst which was prepared by incipient wet impregnation method was employed in the partial oxidation glycerol reforming reaction at 700 °C and carbon to oxygen ratio of 0.9 resulted in hydrogen selectivity of 79% and 100% glycerol conversion without any traces of carbon deposition after 10 h time-on-stream. The high selectivity attained by ceria modified Al_2O_3 supported Rh catalyst was attributed to the dominance of the surface reactions whereby the adsorption of all the hydroxy-containing compounds was insinuated to be bonded on the Rh surfaces as an alkoxide-based compound that decomposes to hydrogen and other C1 products. In a similar study, Liu and Lin [103] reported the conversion of glycerol by partial oxidation reforming using Pt-, $LaMnO_3$-, and $Pt/LaMnO_3$-coated monoliths catalysts. The partial oxidation reforming of the catalysts over the catalysts revealed that the Pt displayed the least activity as a result of sintering. Whereas, the $Pt/LaMnO_3$ catalyst was found to display the highest activity with hydrogen selectivity of 90%. The better performance of the $Pt/LaMnO_3$ catalyst was attributed to the synergistic effect of Pt sintering suppression and the good interaction between the Pt and the $LaMnO_3$ [106]. The speedy oxygen consumption and high-temperature nature of the partial oxidation glycerol reforming often result in the formation of various parallel reactions [107]. In comparison with the steam glycerol reforming, the formation of carbon in the partial oxidation glycerol reforming is lower due to the oxidative environment which invariably could lead to long time-on-stream [100]. In this regard, an increase in the supply of oxygen during the partial oxidation glycerol reforming reaction could enhance the reduction of carbon deposition on the surface of the catalyst due to the gasification of the carbon [108].

Although partial oxidation of glycerol has a great potential to be used for the production of hydrogen on a large scale, however, the high temperature resulting from the exothermic reaction is a major constraint. In addition, low yield of hydrogen is often obtained from the partial oxidation glycerol reforming. In other to overcome these challenges, it is required to use materials that can withstand high temperature during the construction of the reactor. Besides, preheating of the feeds and application of thermal integration concepts to the flow streams could significantly help in overcoming the challenges of high temperature. Moreover, design and synthesis of suitable catalysts that can be employed in the glycerol partial oxidation reforming could help to improve the hydrogen yield and lower the operating temperature of the reaction.

Auto-thermal reforming of glycerol

The autothermal glycerol reforming technique for hydrogen production involves the combination of the steam glycerol reforming and the partial oxidation glycerol reforming reactions as shown in Equations (16–20) [37]. As stated earlier, the steam glycerol reforming has the constraints of catalyst deactivation and high energy demand. Whereas, the partial oxidation glycerol reforming is an exothermic reaction which is constraint by low hydrogen yield and formation of hot spots [109]. Hence, the combination of these two techniques would result in dual advantages of high energy efficiency and process stability [34]. Although, the auto-thermal reforming concept has been in use for many years, however, its application to reforming of glycerol for hydrogen production is a relatively new technique with a paltry research interest in the past one decade. Besides being a potential technique for industrial-scale hydrogen production, the autothermal glycerol reforming can also be used for the production of syngas with low H_2: CO ratio which can be used as chemical intermediates for the synthesis of liquid hydrocarbons [110,111]. The auto-thermal glycerol reforming has a great potential for production of hydrogen on an industrial scale since the existing technology being used in the auto-thermal methane reforming by Sasol in South Africa can be adapted.

Nevertheless, there are several technical issues that have been identified to impede the development of the techniques. One of such issues is the lack of proper understanding of the mechanisms of catalytic deactivation viz. carbon formation and deposition [109]. Studies have shown that carbon formation is facilitated in the combustion chamber of the auto-thermal reformer at temperature greater than 800 °C [112]. Due to the high temperature, there is a tendency for the formation of precursor to the carbon, but the rate-controlling steps of the deactivation mechanism are yet to be ascertained [113]. To solve the challenges of catalyst deactivation by carbon deposition, it has been proposed that the excess steam supply at the high-temperature reaction zone of the reformer could facilitate the oxidation of the carbon thereby reducing the rate of carbon deposition [34].

Up to date, there are scanty experimental studies on the auto-thermal glycerol reforming compare to several published works on the thermodynamics studies. Abdul Ghani et al. [37] investigated the use of promoted cerium-zirconium supported Ni-catalyst in auto thermal glycerol reforming for hydrogen production. The Mg, Ca and Gd promoted cerium-zirconium supported Ni-catalysts were synthesized using wet impregnation method and tested in the auto thermal glycerol reforming reaction at varying reaction temperature (S/C) (550–650 °C), steam to carbon ratio (1.6–3.6) and oxygen to carbon ratio (O/C) (0.2–0.8). The findings revealed that at reaction temperature of 600 °C, SC ratio of 3.6 and OC ratio of 0.6, the highest hydrogen selectivity of 75%, 78%, and 77% were obtained for 5 wt%Ni-Mg/CeZr, 5 wt%Ni-Ca/CeZr, and 5 wt%Ni-Gd/CeZr catalysts, respectively. At the same conditions, glycerol conversion of 78%, 85% and 84% were also obtained for 5 wt%Ni-Mg/CeZr, 5 wt%Ni-Ca/CeZr and 5 wt%Ni-Gd/CeZr catalysts, respectively. It is obvious that the catalytic performance was significantly influenced by the addition of the different promoters, although the catalytic performance of the unpromoted 5%Ni/CeZr was not presented in the study. The study also revealed that the variation in process parameters such as the reaction temperature, the steam to carbon ratio, oxygen to carbon ratio, and the calcination temperature of the catalysts significantly influence the catalytic performance in terms of hydrogen production and the glycerol conversion. Hydrogen production during the auto-thermal

glycerol reforming was observed to increase with the increase in the reaction temperature as a result of the endothermic nature of the steam reforming component of the autothermal reaction. Calcination temperature higher than 550 °C was reported to significantly reduce the catalytic performance of the catalysts probably due to the agglomeration of the catalyst nanoparticles. In terms of the variation in the oxygen to carbon ratio, the addition of oxygen was reported to enhance the energy efficiency of the reaction through heat supply by oxidation. Moreover, the stability of the catalyst was enhanced through the gasification of the carbon deposited. Nevertheless, caution must be taken in the variation of the oxygen with the carbon ratio in order to prevent hot zone and the depletion of hydrogen production at high oxygen concentration. The variation in the steam-to-carbon ratio was also reported to significantly affect hydrogen production during autothermal glycerol reforming [114]. Studies have shown that excess steam during the autothermal glycerol reforming reaction helps in suppressing methanation, reduce carbon deposition over the catalysts, and also improve hydrogen production [112,113].

$$C_3H_8O_3 + 3H_2O \leftrightarrow 3CO + 7H_2 \quad \Delta H > 0 \tag{15}$$

Glycerol oxidation

$$C_3H_8O_3 + 0.5O_2 \leftrightarrow 2CO + 4H_2 + CO_2 \quad \Delta H > 0 \tag{16}$$

$$C_3H_8O_3 + O_2 \leftrightarrow CO + 4H_2 + 2CO_2 \quad \Delta H > 0 \tag{17}$$

$$C_3H_8O_3 + 1.5O_2 \leftrightarrow 4H_2 + 3CO_2 \quad \Delta H > 0 \tag{18}$$

$$C_3H_8O_3 + 3.5O_2 \leftrightarrow 4H_2O + 3CO_2 \quad \Delta H > 0 \tag{19}$$

$$6H_2 + 3CO \leftrightarrow C_2H_6 + 3H_2O \quad \Delta H < 0 \tag{20}$$
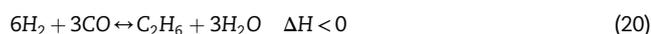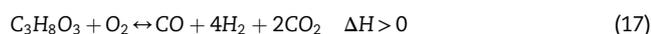
Aqueous phase reforming of glycerol

Hydrogen can be produced by aqueous phase reforming of glycerol via the catalytic conversion of glycerol in water as depicted in Fig. 5. The aqueous phase reforming of glycerol gives products in two different phases (liquid and gaseous) which are often collected separately. The main product of the gaseous is H_2 which is often accompanied by other gaseous by-products such as CO_2, CO, CH_4, and C_3H_8 [115]. While the liquid product stream consists of a complex mixture of hydrocarbon and oxygenated hydrocarbons. Compare with glycerol reforming using steam and CO_2 which required high thermal energy, the energy requirement in aqueous phase reforming of glycerol is reduced through the elimination of

the necessity to produce steam (as in the case of steam reforming) or high temperature needed to vaporize the glycerol (as in the case of O_2 and CO_2 reforming) [116]. Moreover, the temperature and pressure range in aqueous phase reforming of glycerol supports water gas shift reaction which enables hydrogen production with low CO content. A typical aqueous phase glycerol reforming reaction occurs at a pressure range of 15−50 bar which allows the efficient separation of the hydrogen gas from other gaseous products by pressure-swing adsorption or membrane technology. Besides the low reaction temperature (200−300 °C) required for the aqueous phase glycerol reforming reaction prevent the occurrence of catalyst deactivation by carbon deposition which usually occurs at temperature > 500 °C. The detail reaction in aqueous phase glycerol reforming is represented in Equations (21)−(26).

The aqueous phase glycerol reforming Equations (20) and the water gas shift reactions (Equation (21)) are the main reactions for hydrogen production while Equations (23)−(26) are the sides reaction such as methanation and Fischer-Tropsch whereby hydrogen is utilized for the production of alkane.

$$C_3H_8O_3 + 3H_2O \leftrightarrow 3CO + 7H_2 \quad \Delta H > 0 \tag{21}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H < 0 \tag{22}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H < 0 \tag{23}$$

$$CO + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H < 0 \tag{24}$$

$$7H_2 + 3CO \leftrightarrow C_3H_8 + 3H_2O \quad \Delta H < 0 \tag{25}$$

$$6H_2 + 3CO \leftrightarrow C_2H_6 + 3H_2O \quad \Delta H < 0 \tag{26}$$
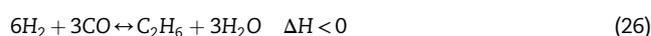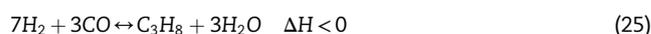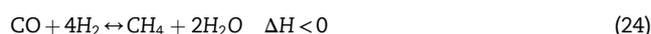
Hydrogen production by aqueous phase reforming of glycerol has been extensively investigated since it was first reported by Cortright and co-workers in 2002 [118,119]. At initial stage between 2002 and 2007, there was little research awareness on aqueous phase reforming of glycerol to hydrogen as evidenced from the literature output. Subsequently, there has been a gradual increase in research interest in hydrogen production by aqueous phase reforming of glycerol.

Table 4 summarize selected reviewed articles on hydrogen production by aqueous phase reforming of glycerol. It can be seen that hydrogen production by aqueous phase reforming of glycerol has been investigated using different types of supported metal catalysts under varying reactor configurations. The catalysts investigated in the selected reviewed paper were
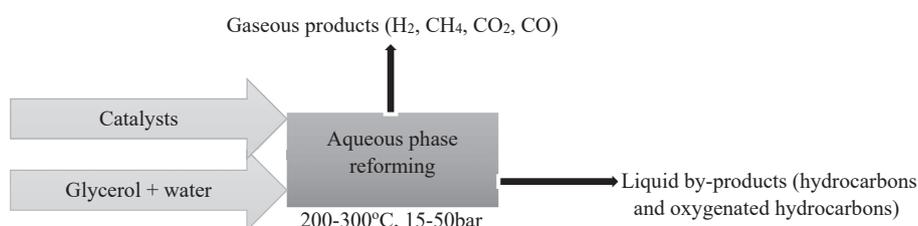

Fig. 5 − Schematic representation of aqueous phase glycerol reforming [117]).

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Table 4 − Summary of selected literature on hydrogen production by aqueous phase reforming of glycerol.

Catalyst	Preparation method	S_{BET} (m^2/g)	Reactor type	Feed/WHSV (h^{-1})	Time on stream (TOS) (h)	Reaction conditions (Temp./pressure)	Conversion (%)	H$_2$ yield (%)/H$_2$/CO ratio	Reference
33%NiAl$_2$O$_4$-300	Co-precipitation	94.9	Fixed bed up flow reactor	10% gly/w,24.5	2	250 °C/45 bar	0.1	0.7/n.r	[120]
33%NiAl$_2$O$_4$-450	Co-precipitation	93.5	Fixed bed up flow reactor	10% gly/w,24.5	2	250 °C/45 bar	0.3	1.4/n.r	[120]
33%NiAl$_2$O$_4$-600	Co-precipitation	89.8	Fixed bed up flow reactor	10% gly/w,24.5	2	250 °C/45 bar	68	12.3/n.r	[120]
33%NiAl$_2$O$_4$-700	Co-precipitation	83.1	Fixed bed up flow reactor	10% gly/w,24.5	2	250 °C/45 bar	90	18.3/n.r	[120]
33%NiAl$_2$O$_4$-850	Co-precipitation	76.7	fixed-bed up-flow reactor	10% gly/w, 24.5	2	250 °C/40 bar	93	21/n.r	[120]
20%Ni-5%Cu/MgO	Co-precipitation	155.7	fixed bed tubular reactor	10% gly/w, 5.0	6	250 °C/35 bar	33	22.6/0.97	[117]
20%Ni-10%Cu/MgO	Co-precipitation	168.9	fixed bed tubular reactor	10% gly/w, 5.0	6	250 °C/35 bar	20	15.1/0.90	[117]
20%Ni/MgO	Co-precipitation	172.9	fixed bed tubular reactor	10% gly/w, 5.0	6	250 °C/70 bar	55	39/1.02	[117]
20%Ni-5%Cu/MgO	Co-precipitation	155.7	fixed bed tubular reactor	10% gly/w, 5.0	6	270 °C/70 bar	80	55.3/1.10	[117]
20%Ni-10%Cu/MgO	Co-precipitation	168.9	fixed bed tubular reactor	10% gly/w, 5.0	6	270 °C/70 bar	62	45/1.11	[117]
65%Ni/SiO$_2$-Al$_2$O$_3$	Commercial	195	Batch reactor	10% pure glycerol	4	240 °C/33.5 bar	45	7.1/n.r	[121]
65%Ni/SiO$_2$-Al$_2$O$_3$	Commercial	195	Batch reactor	20% pure glycerol	4	240 °C/33.5 bar	40	3.8/n.r	[121]
65%Ni/SiO$_2$-Al$_2$O$_3$	Commercial	195	Batch reactor	40% pure glycerol	4	240 °C/33.5 bar	30	3.7/n.r	[121]
1%Pt/CeO$_2$-Al$_2$O$_3$	Wet impregnation	149	Continuous-flow fixed-bed reactor	1% gly/w, 12.0	2	240 °C/40 bar	87	60/0.95	[122]
6%Ni/CeO$_2$-Al$_2$O$_3$	Wet impregnation	125	Continuous-flow fixed-bed reactor	1% gly/w, 12.1	2	240 °C/40 bar	59	35/0.67	[122]
1%Pt-3%Ni/CeO$_2$-Al$_2$O$_3$	Wet impregnation	139	Continuous-flow fixed-bed reactor	1% gly/w, 12.2	2	240 °C/40 bar	96	86/1.03	[122]
1%Pt-6%Ni/CeO$_2$-Al$_2$O$_3$	Wet impregnation	120	Continuous-flow fixed-bed reactor	1% gly/w, 12.3	2	240 °C/40 bar	93	69/1.20	[122]
1%Pt-12%Ni/CeO$_2$-Al$_2$O$_3$	Wet impregnation	116	Continuous-flow fixed-bed reactor	1% gly/w, 12.4	2	240 °C/40 bar	87	66/0.97	[122]
1%Pt-18%Ni/CeO$_2$-Al$_2$O$_3$	Wet impregnation	109	Continuous-flow fixed-bed reactor	1% gly/w, 12.5	2	240 °C/40 bar	26	12/1.02	[122]
10%Ni/CeO$_2$	Co-precipitation	19	Fixed bed reactor	10% gly/w, 2.45	2	250 °C/20 bar	62	67/n.r	[126]
10%Ni/Ce$_{0.7}$Zr$_{0.3}$O$_2$	Co-precipitation	69	Fixed bed reactor	10% gly/w, 2.46	2	250 °C/20 bar	87	56/n.r	[126]
10%Ni/Ce$_{0.5}$Zr$_{0.5}$O$_2$	Co-precipitation	70	Fixed bed reactor	10% gly/w, 2.47	2	250 °C/20 bar	88	52/n.r	[126]
10%Ni/Ce$_{0.3}$Zr$_{0.7}$O$_2$	Co-precipitation	72	Fixed bed reactor	10% gly/w, 2.48	2	250 °C/20 bar	90	49/n.r	[126]
10%Ni/ZrO$_2$	Co-precipitation	15	Fixed bed reactor	10% gly/w, 2.49	2	250 °C/20 bar	55	63/n.r	[126]
20%Ni/CeO$_2$	Wet impregnation	62	Auto-clave batch reactor	10 wt% glycerol	6	270°/1 bar	~72	~25/6.8	[124]
20%Ni/CeO$_2$	Co-precipitation	51	Auto-clave batch reactor	10 wt% glycerol	6	270°/1 bar	~78	~18/6.7	[124]

n.r: not reported.

mostly prepared using co-precipitation and wet-impregnation methods. The as-prepared catalysts were tested in aqueous phase reforming of glycerol using reactor configuration such as fixed-bed flow reactor and batch reactor. The reaction temperature and pressure employed for the aqueous phase reforming of glycerol varies between 250 and 270 °C and 1−70 bar respectively. It can be seen that the catalytic performance of the various catalysts used in the aqueous phase glycerol reforming is to a large extent dependent on the reduction temperature, metal loading, nature of support, addition of promoter, synthesis method and the reaction conditions. Supported Ni and Pt catalysts have been extensively investigated for hydrogen production by aqueous phase glycerol reforming. The effect of reduction temperature on the activity of nickel aluminate ($NiAl_2O_4$) in aqueous phase glycerol reforming was investigated by Morales-Marín et al. [120]. The $NiAl_2O_4$ catalyst synthesized by co-precipitation was reduced at a temperature range from 300 to 850 °C and utilized for hydrogen production in aqueous phase glycerol reforming at 250 °C and 45 bar. The findings revealed that the performance of the $NiAl_2O_4$ catalysts in term of hydrogen yield and glycerol was significantly dependent on the reduction temperature. The hydrogen yield and the glycerol conversion increase with the increase in the reduction temperature with the highest glycerol conversion of 93% and hydrogen yield of 23% obtained from the $NiAl_2O_4$ catalyst reduced at 850 °C. The performance of the $NiAl_2O_4$ catalyst reduced at 850 °C can be attributed to the complete reduction of the Ni species and thereby increasing the concentration of the active Ni site for the aqueous phase glycerol reforming. In a similar study by Manfro et al. [117], the effect of Cu addition and loading on the activity of Ni/MgO catalysts in aqueous phase glycerol reforming was investigated. The Ni/MgO catalyst was synthesized by co-precipitation method with a variation of Cu contents from 5 to 10 wt%. The catalysts which include 20 wt% Ni/MgO, 20%wtNi-5%Cu/MgO and 20 wt%Ni-10%Cu/MgO were tested under two different reaction conditions (250 °C/35 bar and 270 °C/70 bar). The finding revealed that the performance of the catalysts in the aqueous phase glycerol reforming were influenced by the Cu contents and the reaction conditions. The 20%Ni/MgO, 20%Ni-5%Cu/MgO and 20%Ni-10%Cu/MgO catalysts were observed to displayed higher activity at 270 °C and 70 bar. The highest catalytic performance (hydrogen yield of 55% and glycerol conversion of 80%) was reported for 20% Ni-5%Cu/MgO. Furthermore, variation in glycerol concentration has been reported to significantly affect hydrogen production during catalytic aqueous phase glycerol reforming as reported by Seretis and Tsiakaras [121]. The authors employed a commercial 65%Ni/SiO_2-Al_2O_3 catalyst for hydrogen production by aqueous phase glycerol reforming with varying glycerol concentration from 10% to 40% at 240 °C and 33.5 bar in a batch reactor. The findings revealed that hydrogen production decreases with increase in the glycerol concentration. Highest hydrogen yield of 7.1% was obtained using 10% glycerol. The decrease in the hydrogen yield as the glycerol concentration increases has been attributed to the corresponding increase in the autogenous pressure of the reaction which favours methanation reaction. Hence, most of the hydrogen produced as the glycerol concentration increases were used up in the methanation reaction. The use of noble metals such

as Platinum as co/bimetallic catalyst has been reported to produce high hydrogen yield during aqueous phase glycerol reforming. Rahman et al. [122]. reported a comparative catalytic activity of Pt/CeO_2-Al_2O_3 and Ni/Pt/CeO_2-Al_2O_3 catalysts in aqueous phase glycerol reforming. The effect of Pt and Ni loading, as well as the effect of bimetallic Pt-Ni on hydrogen production, was investigated. The study revealed that the Pt/CeO_2-Al_2O_3 catalysts under the same experimental conditions showed a superior performance (glycerol conversion of 87% and hydrogen yield of 60%) compared with the Ni/Pt/CeO_2-Al_2O_3 catalysts (glycerol conversion of 59% and hydrogen yield of 35%). However, greater synergistic effects of using the bimetallic Pt-Ni/CeO_2-Al_2O_3 catalyst was observed resulting in glycerol conversion of 96% and hydrogen yield of 86%. An increase in the Ni content of the bimetallic Pt-Ni/CeO_2-Al_2O_3 from 3% to 12% was found to gradually reduce the glycerol conversion from 96% to 87% and the hydrogen yield from 86% to 66% which is primarily due to the sintering of the Ni species at high loading which is consistent with the work of Bai et al. [123]. In addition to the use of bimetallic catalysts, the preparation method has been found to have a significant influence on catalytic activity during aqueous phase glycerol reforming. The effect of synthesis techniques on the catalytic activity of 20 wt%Ni/CeO_2 catalyst in aqueous phase glycerol reforming has been reported by Manfro et al. [124]. The authors employed wet-impregnation and co-precipitation methods for the synthesis of 20 wt%Ni/CeO_2 catalyst and tested the catalytic activity in aqueous phase glycerol reforming in an autoclave batch reactor. The findings show that the 20%wtNi/CeO_2 catalyst prepared by wet impregnation method displayed higher activity in terms of hydrogen yield (25%) compared with the 20 wt%Ni/CeO_2 catalyst prepared by co-precipitation method (hydrogen yield of 18%).

It can be seen that aqueous phase glycerol reforming is a promising technical route for scale-up hydrogen production, although catalytic performance during the reaction strongly dependent on several factors which have been discoursed above. Besides being a prospective technological route for hydrogen production, aqueous phase glycerol reforming is also a potential means of producing syngas that can be used as chemical intermediates for the production of valuable chemicals. One major challenge of the hydrogen production from aqueous phase glycerol reforming which needs research focus is how to minimize the influence of side reactions such as methanation and Fischer-Tropsch reactions during which the hydrogen produced is used up for production of alkanes and olefins [125].

Photocatalytic reforming of glycerol

Besides the conventional thermal-catalytic methods of converting glycerol to hydrogen, the photocatalytic reforming is an alternative technique for renewable hydrogen production from biomass-derived glycerol [127,128]. The photocatalytic reaction involves the conversion of glycerol in the presence of a photocatalyst at ambient/low temperature [129]. During this reaction, photo-induced holes (h+) acts as oxidants used for the conversion of glycerol while the induced electrons act as reductants for reducing H+ to H_2 [130]. The photocatalytic glycerol reforming has dual advantages of not requiring high

energy demands and none occurrence of catalytic deactivation since the reaction occurs at low temperature [131]. Several authors have reported the use of photocatalytic glycerol reforming to hydrogen as reported in a mini-review by Stelmachowski et al. [132]. Jiang et al. [130] investigated hydrogen production by photocatalytic reforming of glycerol over Pt/TiO$_2$ photocatalyst. The photocatalytic glycerol reforming which was performed at room temperature resulted in the evolution of 2.25 mmol hydrogen after 5h irradiation time. Mizukoshi [133] investigated the effect of sonification on hydrogen production by photocatalytic glycerol reforming over deuterium modified Pt/TiO$_2$ photocatalyst. The photocatalytic reaction resulted in the evolution of 400 μmol of hydrogen after 2 h irradiation time under UV-illuminated system. It was inferred that the photocatalytic reaction was enhanced by the sonification of the UV-illuminated system resulting in higher evolution of hydrogen. In a similar study, Sadanandam et al. [134] investigated hydrogen production by photocatalytic glycerol reforming considering the effects of TiO$_2$ calcination temperature, Ag loading, photocatalyst content, light source on the hydrogen production. The study revealed that the highest hydrogen production of 7030 μmol g^{-1}h^{-1} was obtained during photocatalytic glycerol reforming over 3% Ag-TiO$_2$. The authors concluded that the interaction of the Ag$_2$O-Ag phases on the nano-TiO$_2$ play significant role in the high hydrogen production during the photocatalytic glycerol reforming.

Although, the photocatalytic glycerol reforming has a very high prospect as a technical route for hydrogen production, nevertheless, the amount of hydrogen production is far less than that obtained from the steam glycerol reforming, dry glycerol reforming and partial oxidation glycerol reforming routes. This demerit might pose a major limitation to the development of the photocatalytic glycerol reforming as a viable alternative for hydrogen production.

Super critical water reforming of glycerol

The production of hydrogen by supercritical water reforming of glycerol is a nascent technology that is attracting research attention in the quest for alternative energy production. Supercritical water is usually obtained at pressure >221 bar and temperature >374 °C [28]. Conducting reforming at the conditions of the supercritical water usually results in the conversion of glycerol to hydrogen and some other associated gases which can easily be separated from the water phase when cooled to room temperature [135]. In supercritical water reforming of glycerol, water serves a dual purpose as the reaction medium and the reactant [28]. The supercritical water reforming of glycerol can either be catalyzed or a non-catalyzed reaction [28]. For a catalyzed supercritical water reforming of glycerol, the reaction usually occurs at low temperature compared to a non-catalyzed process where the reaction occurs at high temperature [136]. Hydrogen production and glycerol conversion by supercritical water reforming are often influenced by feed concentration, operating conditions and whether the reaction is catalyzed or not. There is a growing research interest in the application of supercritical water reforming of glycerol for hydrogen production. A brief review on glycerol reforming in supercritical water by
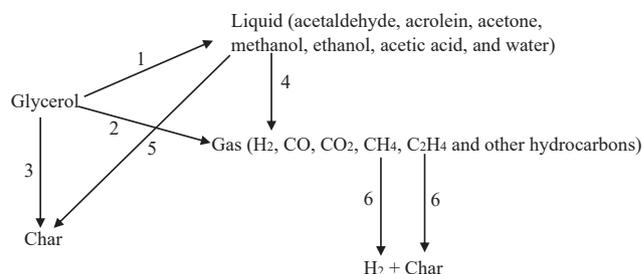

Fig. 6 – The concurrent and consecutive reaction pathways of glycerol pyrolysis [143].[1]

Markocic et al. [28] revealed that supercritical water has been employed for glycerol reforming using catalysts such as NaHSO$_4$, H$_2$SO$_4$, ZnSO$_4$, Ru/TiO$_2$, Ru/ZrO$_2$ and NaOH at different reaction conditions. The various experimental studies revealed that, glycerol reforming in supercritical water resulted in hydrogen and other wide range of by-products. The product distributions were observed to be influenced by variation in parameters such as temperature, pressure, feed ratio, reaction time or type of catalyst.

Ortiz et al. [137] reported the production of hydrogen by supercritical water reforming of glycerol over Ru/Al$_2$O$_3$ and Ni/Al$_2$O$_3$-SiO$_2$ catalysts at 240 bar and temperature range of 500–800 °C in a tubular fixed-bed reactor. The highest hydrogen yield of 71% was obtained at 800 °C during the supercritical water reforming over the over Ru/Al$_2$O$_3$ compared to the 51.59% obtained over Ru/Al$_2$O$_3$ catalyst. Besides, in the absence of catalyst hydrogen yield of 48.5% was obtained during the supercritical water reforming of glycerol. It was observed that methanation was a major competing reaction during the supercritical water reforming reaction which was majorly responsible for the reduction of hydrogen yield.

A recent study on hydrogen production by supercritical water reforming of glycerol was reported by Patcharavorachot et al. [136]. The study revealed that hydrogen production by supercritical water reforming of glycerol can be optimized by using the appropriate values of parameters such as temperature, pressure, and catalyst to glycerol ratio. Maximum hydrogen production during the supercritical water reforming of glycerol over CaO catalyst was obtained at 450 °C, 243 bar and CaO to glycerol ratio of 2.5.

Although the catalyzed supercritical water reforming seems to have great potential as a technical route for hydrogen production, one major challenge is carbon formation and deposition that often results in catalyst deactivation and plugging of the reactor. However, in order to reduce the impact of this challenge on the efficiency of the process, it has been suggested by different authors that the supercritical reforming should be performed at short residence time, low feed concentration and high temperature.

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[1] 1. conversion of glycerol to liquid products 2. conversion of glycerol to gaseous products 3. Conversion of glycerol to chars 4. conversion of liquid products obtained from glycerol to gaseous products 5. Conversion of the liquid products obtained from glycerol to char 6. Conversion of the gaseous products to hydrogen and char.

Catalyst	Synthesis method	Type of reactor	Reaction condition	S_{BET} (m^2/g)	Glycerol conversion (%)	Hydrogen yield (%)/H_2/CO ratio	References
20%Ni/Al$_2$O$_3$	Wet impregnation	Fixed bed reactor	700–800 °C, TOS:3h WHSV $= 4.5 \times 10^4$ ml g^{-1} h^{-1}	7.2	23.27	26.01/n.r	[147]
3%La-20%Ni/Al$_2$O$_3$	Wet impregnation	Fixed bed reactor	700–800 °C, TOS: 3h WHSV $= 4.5 \times 10^4$ ml g^{-1} h^{-1}	2.89	27.3	26.21/1.3	[147]
3%Pr-20%Ni/Al$_2$O$_3$	Wet impregnation	Fixed bed reactor	700–800 °C, TOS:3h WHSV $= 4.5 \times 10^4$ ml g^{-1} h^{-1}	n.r	n.r	29.04/1.87	[142]
3%Sm-20%Ni/Al$_2$O$_3$	Wet impregnation	Fixed bed reactor	700–800 °C, TOS:3h WHSV $= 4.5 \times 10^4$ ml g^{-1} h^{-1}	2.68	28.35	27.43/1.70	[146]
3%Ce-20%Ni/Al$_2$O$_3$	Wet impregnation	Fixed bed reactor	700–800 °C, TOS:3h WHSV $= 4.5 \times 10^4$ ml g^{-1} h-1	2.89	30.17	28.52/1.50	[141]
Non-catalyzed	n.a	Batch reactor	750–800 °C, TOS: 30 min	n.a	24	39/0.90	[145]
Non-catalyzed	n.a	Fixed bed reactor	650–800 °C, TOS: 30 min	n.a	27.7	n.r	[145]
Activated carbon-BC	n.a	Electric furnace	400–900 °C, TOS:n.r	n.a	n.r	28.9/0.6	[148]
Activated carbon-BC	n.a	Microwave oven	800 °C, TOS:n.r	n.a	n.r	34.6/0.8	[148]
Activated carbon-CC	n.a	Electric furnace	400–900 °C, TOS:n.r	n.a	n.r	30.1/0.7	[148]
Activated carbon-CC	n.a	Microwave oven	800 °C, TOS:n.r	n.a	n.r	33.2/0.9	[148]
Non-catalyzed	n.a	Electric furnace	800 °C, TOS:n.r	n.a	n.r	22.6/0.6	[148]

BC: Bituminous Carbon, CC: Carbonaceous Catalyst, n.a: not applicable, n.r: not reported.

Pyrolysis of glycerol

Typically, pyrolysis is a thermal process that involves the conversion of biomass such as glycerol to char, liquid and gaseous products in an inert atmosphere [138]. The conversion of the biomass to liquid products is favoured at low-temperature range (400–600 °C) while the conversion of the biomass to gaseous products is favoured at high temperature (>750 °C) [139]. The pyrolysis of glycerol involves the thermal conversion of glycerol at high temperature to hydrogen, other gaseous products such as CO, CO_2 and CH as well as liquid hydrocarbons [140]. The pyrolysis process can either be catalyzed or non-catalyzed [138,141]. Studies have shown that conversion of pyrolysis is often accompanied by a series of complex reactions which culminate in product formation [142]. In line with this, Valliyappan et al. [143] in their study proposed a series of reaction pathway for the non-catalytic pyrolysis of glycerol as shown in Fig. 6. The authors proposed that product formation during non-catalytic pyrolysis of glycerol often occurs with concurrent reactions, consecutive reaction, dehydration and cracking reactions. The concurrent and dehydration reactions (1)–(3) which occurs at low temperature often result in the conversion of glycerol to liquid, gas and char. While the consecutive and thermal cracking reactions ((4), (5), and (6)) which occur at high-temperature results in the formation of H_2, CO and char. Hydrogen production via glycerol pyrolysis is relatively a new area of research, although there are few existing industrial-scale biomass pyrolysis such as Ensyn, Canada (2 × 45 te/day, CFB), pyrovac Canada, 35 te/day, Fortnum/Vapo, Finland (12 te/day) and Dynamotive, Canada (10 te/day) [144].

Several authors have reported the application of non-catalytic and catalytic pyrolysis of glycerol for hydrogen production as shown in Table 5. Valliyappan et al. [143] reported the non-catalytic pyrolysis of glycerol in a continuous down-flow fixed-bed at a temperature range of 650–800 °C. The findings show that the glycerol pyrolysis products mainly consist of hydrogen and other gaseous products such as CO, CO_2, CH_4 and C_2H_2. Factors such as pyrolysis temperature, carrier flow rates, the particle diameter of packing materials were found to significantly influence the product distributions and the glycerol conversion. The highest hydrogen yield of 48% was obtained at 800 °C. In a similar study, Fantozzi et al. [145] studied the non-catalytic pyrolysis of glycerol in a batch reactor at a temperature range of 750–800 °C. Hydrogen yield between 44 and 48% was obtained from the glycerol pyrolysis. One major challenge often encountered during the non-catalytic pyrolysis process is the decrease in the yield of the gaseous products as the carrier gas flow rate is increased which invariably favours an increase in liquid yield. In addition, the increase in the gas flowrates has been found to also results in the decrease in the residence time which also reduce the glycerol conversion and favours the liquid products.

For the catalytic glycerol pyrolysis, the thermal decomposition of glycerol under an inert atmosphere occurs in the presence of a catalyst. Shahirah et al. [141] studies the catalytic glycerol pyrolysis over Cerium promoted Ni/Al$_2$O$_3$ catalyst prepared by the wet impregnated method in a fixed bed tubular reactor at a reaction temperature of 700–800 °C. The catalytic glycerol pyrolysis over the Cerium promoted Ni/Al$_2$O$_3$ resulted in the highest hydrogen yield of 26.21% at 800 °C. Also, the use of praseodymium (Pr) and samarium (Sm)

to promote the activity of Ni/Al$_2$O$_3$ catalyst in pyrolysis of glycerol under the same reaction conditions has been reported [40,146]. The catalytic activity of Pr-Ni/Al$_2$O$_3$ and the Sm-Ni/Al$_2$O$_3$ catalysts in the glycerol pyrolysis resulted in the highest hydrogen yield of 29.04% and 28%, respectively. In a follow-up study, Shahirah et al. [147] employed lanthanum (La) promoted Ni/Al$_2$O$_3$ catalyst prepared using wet impregnation method in glycerol pyrolysis to hydrogen at a temperature range of 700−800 °C. The results revealed that hydrogen yield increases with increases in temperature. The highest hydrogen yield of 32.30% was obtained at 800 °C. The promoted catalysts were found to have better catalytic performance compared to the unpromoted one. The effect of using different reactor configurations and catalysts have been investigated by Ng et al. [45]. The authors employed activated carbon prepared from carbonaceous carbon and coconut shell as catalysts for the glycerol pyrolysis. The catalytic performance of the catalysts was tested in an electric furnace reactor and microwave-assisted reactor at a temperature range of 400−800 °C. The results revealed that the activated carbon used as a catalyst in the pyrolysis reaction produced a high hydrogen yield of 34.6%. The higher hydrogen yield obtained during the glycerol pyrolysis in the microwave reactor was attributed to the hot spot generated by the microwave. Moreover, the hydrogen yield obtained from the catalyzed glycerol pyrolysis was found to be higher than the uncatalyzed reaction which can be attributed to the synergistic effect of the catalyst in breaking the energy barrier during the glycerol pyrolysis reaction. Despite the prospect of the catalytic pyrolysis of glycerol as one of the feasible technical routes for hydrogen production, catalyst deactivation by carbon deposition and reactor blockage are major issues researcher are still battling with. Several research efforts in the area of development of highly stable catalyst, optimizing the reactor configuration and conditions are being made to proffer workable solutions to these challenges. In addition to being a potential technical route for hydrogen production, glycerol pyrolysis can also be employed for the production of syngas with low H$_2$: CO ratio which can be used in synthetic fuel production. However, one major challenge that needs research focus is how to obtain pure syngas which is devoid of impurities.

Effect of operating parameter on hydrogen production

Hydrogen production by thermo-catalytic conversion of glycerol has been reported to be influenced by various operating parameters such as reaction temperature, glycerol concentration in the feed and weight hourly space velocity (WHSV). An increase in the reaction temperature during the thermo-catalytic conversion of glycerol often leads to a corresponding increase in the glycerol conversion and hydrogen yield as shown in Fig. 7 [38,62]. This can be explained in terms of the Arrhenius concepts for a temperature-dependent reaction which stipulated that increase in temperature generally leads to an increase in the rate of reactant conversion and product formation. Adhikari et al. [38] and Bobadilla et al. [62] reported the increase in hydrogen yield obtained by glycerol steam
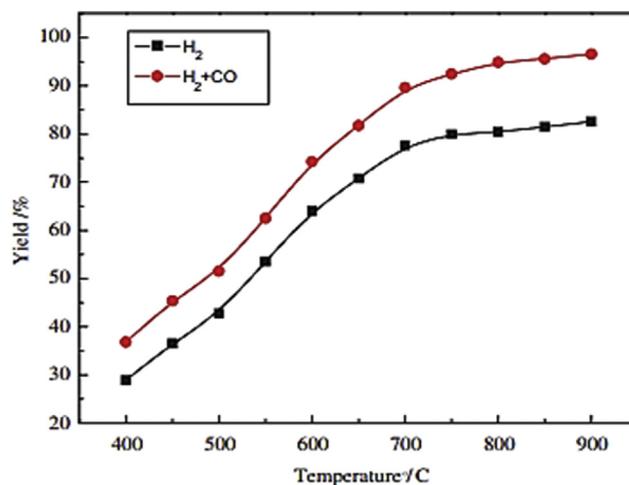

Fig. 7 − Effect of temperature on hydrogen yield obtained from steam reforming of glycerol (Reprinted with permission [149] (Copyright 2016 Taylors & Francis Group).

reforming over bimetallic NiSn/CeO$_2$−MgO−Al$_2$O$_3$ and CeO$_2$, MgO, TiO$_2$ supported Ni catalysts at 600−750 °C (30 °C interval) and 550−650 °C. However, the liquid phase conversion was observed to decrease with increase in temperature whereas the gas-phase conversion was found to increase with temperature. These trends have been attributed to the production of condensable products through a series of side reactions such as dehydration, dehydrogenation and hydrogenolysis reactions. Besides temperature, glycerol concentration feeds (water to glycerol molar ratio or steam to carbon ratio) have also been reported to significantly affect glycerol conversion and hydrogen yield during thermo-catalytic processes as shown in Fig. 8 [38,149]. Studies have shown that the higher the concentration of glycerol in the feed, the lower the hydrogen yield and the glycerol gas-phase conversion. Hydrogen yield and glycerol conversion were reported to increase with an increase in the water to glycerol molar ratios (6:1−12:1). Although, increase in the water-to-glycerol molar ratio significantly improve hydrogen production as well as preventing coke formation on the catalysts, substantial amounts of energy are required for the reforming process due to increase in the amount of water in the feed. Also, weight hourly space velocity has been reported as one of the key parameters that influence hydrogen production by thermo-catalytic conversion of glycerol. Several studies have shown that an increase in the WHSV often resulted in a decrease in hydrogen yield as depicted in Fig. 9 [149,150]. The increase in the WHSV has also been reported to reduce the residence time hence reduced the liquid phase glycerol conversion and thereby affecting the catalyst stability.

Comparative analysis of the different thermo-catalytic conversion techniques for hydrogen production techniques

The comparative analysis of glycerol conversion to hydrogen by different thermo-catalytic processes has been investigated
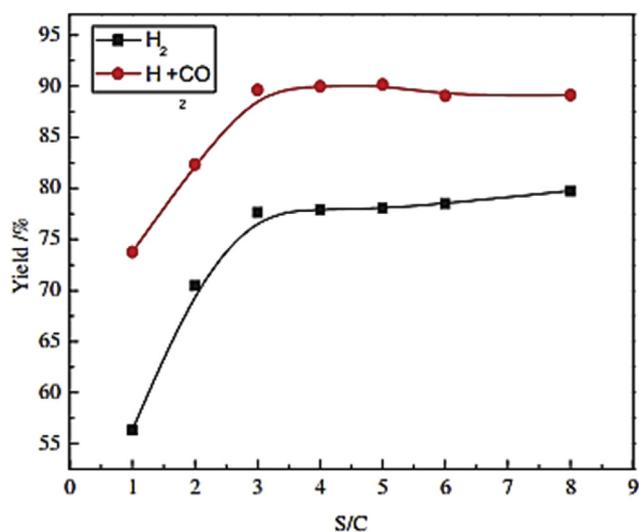
Fig. 8 — Effect of S/C ratio on hydrogen yield obtained from steam reforming of glycerol (Reprinted with permission [149] (Copyright 2016 Taylors & Francis Group).
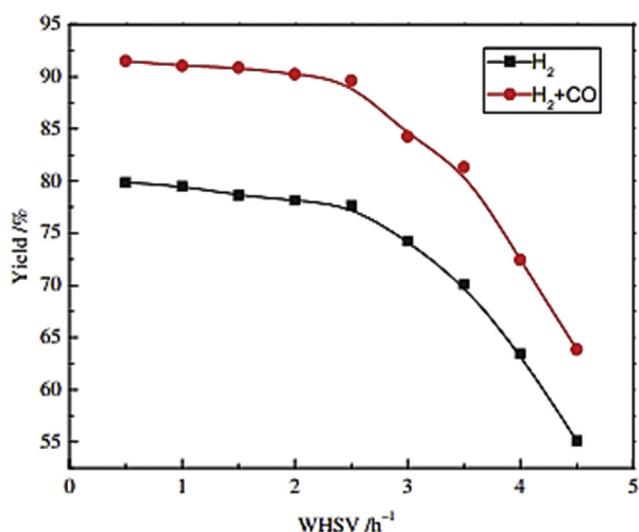

Fig. 9 — Effect of WHSV ratio on hydrogen yield obtained from steam reforming of glycerol (Reprinted with permission [149] (Copyright 2016 Taylors & Francis Group).

by Fernández et al. [148]. Thermo-catalytic processes such as steam reforming, dry reforming and pyrolysis were employed for the conversion of glycerol to hydrogen using a commercial activated carbon catalyst in conventional (electric furnace) and microwave reactors at a temperature range of 400–800 °C. In all cases, it was found that higher hydrogen yield was obtained from the conversion of the glycerol using the microwave reactor compared to the conventional reactor. Moreover, the microwave heating produces a hot zone which facilitates the higher conversion of glycerol to hydrogen. Analysis of the three methods employed for the glycerol conversion showed that steam reforming of glycerol over the activated carbon

catalyst resulted in the highest hydrogen yield compared to the dry glycerol reforming and catalytic pyrolysis. Whereas, the least hydrogen yield was obtained from the dry glycerol reforming. The highest hydrogen yield produced by the steam glycerol reforming was attributed to the contribution of hydrogen from the water. In the steam glycerol reforming, an increase in the water-to-glycerol ratio resulted in the corresponding hydrogen yield. The lowest hydrogen yield obtained from the pyrolysis was attributed to the sole presence of glycerol in the feed compared to steam and dry glycerol reforming which have water and CO_2 in the feed. Overall, glycerol reforming process using water and CO_2 were found to facilitate higher glycerol conversion that the pyrolysis process.

Recently, Patcharavorachot et al. [136] reported a comparative study on hydrogen production by steam glycerol reforming, autothermal glycerol reforming, and supercritical glycerol reforming under the influence of different parameters such as temperature, pressure, steam to glycerol ratio, calcium oxide to glycerol ratio, air to glycerol ratio, and nickel oxide to glycerol ratio. The results revealed that maximum hydrogen production with the highest purity was obtained from the steam glycerol reforming. However, it was observed that both autothermal reforming and chemical looping reforming of glycerol have the capability to function under thermal self-sufficient condition.

The prospects and technical challenges of the different thermo-catalytic conversion of glycerol to hydrogen are summarized in Table 6. The different prospect and technical challenges encountered in the different processes is a function of their respective reaction conditions and the availability of the existing technology that can be adapted. Hydrogen production by steam glycerol reforming, dry glycerol reforming, partial oxidation reforming of glycerol, autothermal reforming of glycerol and pyrolysis of glycerol have major challenges of catalyst deactivation by carbon deposition and reactor blockage. The catalyst deactivation during these processes has been reported to originate from competing reactions such as methane cracking and Bouduoard. Besides, high thermal energy is required for the production of the steam needed for the steam glycerol reforming. Nevertheless, process such as steam glycerol reforming, partial oxidation glycerol reforming, autothermal glycerol reforming and pyrolysis of glycerol can be developed into a fully matured technology process for hydrogen production by modification and adapting the existing technologies that are presently being utilized for hydrogen production via steam methane reforming, autothermal methane reforming, partial oxidation methane reforming and gasification of biomass. Hydrogen production by aqueous phase glycerol reforming is challenged with low selectivity to hydrogen due to low temperature, high methanation reaction. However, these challenges can be overcome by developing catalysts with high selectivity towards hydrogen and minimize side reactions such as methanation. Although, there are no existing technologies that can be modified or adapted for speedy industrial-scale development of the aqueous phase glycerol reforming for hydrogen production, the maturity of the process can be attained in medium-term due to the simplicity of the reaction and lack issues with catalyst deactivation.

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Table 6 — Summary of the prospects and challenges of hydrogen production from the different thermo-catalytic conversion of glycerol.

Thermo-catalytic glycerol conversion technique	Reactions conditions	Industrial-scale prospect/Maturity	Technical challenges
Steam reforming of glycerol	1–10 bar, 600–1000 °C	The existing technology used for hydrogen production by steam methane reforming can be adapted for rapid industrial-scale development/Near term	High energy requirement for steam production and catalyst deactivation by carbon deposition
Dry reforming of glycerol	1 bar, 500–900 °C	Due to the lack of existing matured technology for dry reforming process, the dry reforming of glycerol might take a long term to achieve maturity.	Catalyst deactivation by carbon deposition.
Aqueous phase reforming of glycerol	1–50 bar, 220–270 °C	Due to the simplicity of the process and lack of issues with catalyst deactivation compare to other reforming process, the technology for hydrogen production by aqueous phase reforming of glycerol might take a medium-term to achieve.	Low selectivity to hydrogen due to low temperature, high methanation reaction.
Partial oxidation reforming of glycerol		The existing technology used for hydrogen production by partial oxidation steam reforming can be adopted for partial oxidation reforming of glycerol	
Autothermal reforming of glycerol	1 bar, 400–600 °C	The existing technology used by Sasol South Africa in the auto-thermal methane reforming can be adapted for rapid industrial-scale development	Catalysts deactivation by carbon deposition. Lack of proper understanding of the mechanisms of catalytic deactivation viz. carbon formation and deposition
Pyrolysis of glycerol	1–5 bar, 400–900 °C	Although there are commercial facilities for biomass gasification, the process might need modification to fit into technicalities of hydrogen production by pyrolysis of glycerol which might tale up to medium term to achieve maturity.	Catalyst deactivation by carbon deposition and reactor blockage.

Conclusion and future research outlook on hydrogen production by thermo-catalytic conversion of glycerol

The focus of this study was to review, analyze and summarize recent developments in the application of thermo-catalytic techniques for the conversion of glycerol to hydrogen. Based on this, recent literature related to the steam glycerol reforming, dry glycerol reforming, partial oxidation glycerol reforming, autothermal glycerol reforming, supercritical water reforming of glycerol, photocatalytic glycerol reforming and pyrolysis of glycerol were reviewed and discussed. The review trend shows that there exists a myriad of research interest in hydrogen production from the different thermo-catalytic processes. Although, it has been established in this study that the different thermo-catalytic glycerol conversion process used for the production of hydrogen is constraint with several technical challenges such as low hydrogen yield, catalyst deactivation, and high energy requirement. Nevertheless, there exists a great opportunity for developing different technologies for hydrogen production despite their various challenges. To a large extent, hydrogen production by glycerol reforming using different oxidants such as steam, CO_2 and O_2 seems to be the most developed and might likely attain industrial-scale development in the near future. One major key issue that might be a point of research focus is the rapid development of the various thermo-catalytic process is catalyst deactivation by carbon deposition. Hence, the research efforts made so far on catalyst design and development needs to be doubled by adopting more improved techniques to design highly stable and active catalysts. One of such strategies is to fully understand the kinetics and mechanisms of the complex reactions that usually occur during the various thermo-catalytic glycerol conversion process. Moreover, optimization strategies using response surface methodology can be utilized to investigate the optimum conditions of the process conditions that favours maximum hydrogen production and minimum carbon formation.

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