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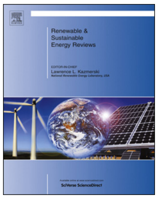

Overview of glycerol reforming for hydrogen production

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ABSTRACT

Hydrogen is used by the chemical industry in numerous processes, and today almost 95% is produced from raw materials based on fossil fuels, such as methane (CH_4). However, catalytic reforming technologies face a number of technical and scientific challenges involving the quality of raw materials, conversion efficiency, and safety issues in the integration of systems of H_2 production, purification and use, among others. Glycerol is a versatile raw material for H_2 production because it is the main by-product of biodiesel production, which a few years ago was consolidated in the world energy matrix and whose production continues to grow in the main consumer markets. Moreover, it has the noteworthy characteristic of decentralized production, which is directly reflected in its easy use. This paper presents a literature review on the reforming technologies applied to glycerol, the advantages of each route, and the main problems involved.

Contents

1. Introduction

Biodiesel was consolidated in the world energy matrix a few years ago and its production continues to grow in the main consumer markets. The European Union is still the largest market, with 12.5 million cubic meters (MCM) produced in 2014, a figure that is predicted to continue up the end of 2015 [1]. The US, another major producer, produced 4.8 MCM in 2014 [2]. In Brazil, biodiesel production in 2014 was 3.1 MCM. In July 2014, the Brazilian government authorized an increase from the previous 5% to 7% in the percentage of biodiesel to be added to diesel for road use, with a projected production of 3.8 MCM by the end of 2015 [3].

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In these markets, biodiesel is produced industrially via transesterification of readily available oil-containing raw materials such as rapeseed in the EU and soybeans in the US and Brazil. The reaction involves mixing the raw material with a short chain alcohol and a catalyst, usually methanol and potassium methoxide, under controlled heating and stirring. At the end of the process, approximately 10 m^3 of glycerol is generated for every 90 m^3 of biodiesel produced [4]. Considering this proportion, more than 2 MCM of glycerol will be obtained in 2015 just from the largest biodiesel producer markets.

In 2013, over 350 thousand tons of glycerol were produced in biodiesel plants in Brazil to meet the domestic demand of 40 thousand tons by the textile, cosmetics and food industries [5,6]. Most of the excess volume was exported, mainly to China, which adds value to the product. In addition, Brazil exported over 230 t of crude glycerol to China in 2014 [7].

Glycerol derived from the biodiesel production process has a dark color and contains variable amounts of soap, catalyst, alcohol (typically methanol), monoglycerides, diglycerides, glycerol oligomers, polymers, water, and unreacted triacylglycerols and biodiesel. This crude glycerol (crude glycerin) contains glycerol concentrations of 40 to 85%, depending on the efficiency of the steps involved in the biodiesel production process. When subjected to a partial purification process involving the addition of mineral acid, the derivatives of fatty acids are removed and the glycerol content increases to 80–85%, and the product contains water, methanol and dissolved salts. Pharmaceutical grade glycerin can be obtained after a distillation process [8–10].

Biodiesel plants normally use crude glycerol to generate energy or to sell, since the cost benefit of purification processes is disadvantageous. An alternative is burning it directly, although the combustion of glycerol is not that simple because it is highly viscous, which greatly hinders the flow, pumping and flame spray process. Its high ignition temperature is also problematic because it reduces the combustion efficiency, resulting in the formation of acrolein, an aldehyde that is highly toxic even at low concentrations. Moreover, the high concentration of residual salts after burning glycerin leads to the formation of deposits and plaque that clog the equipment used in this process. These problems of acrolein formation can be overcome by a preheating step followed by the addition of an auxiliary fuel in burning [11–13].

On the other hand, much of the glycerol that is not used for burning is treated by the dewatering process in a controlled environment for the formation of acrolein as a standard product. When produced, purified and stored, acrolein becomes a product with high added value, since it is an important intermediate for the agricultural and chemical industries. The conventional acrolein production process involves the oxidation of petroleum-based propylene derivatives [14].

Glycerol is also used in pyrolysis and gasification processes that are carried out between 600 and 850 °C, which represent options to partially oxidize the fuel or convert it into another one of higher quality and energy content, such as synthesis gas, which is a mixture of gases (mainly H_2 and CO) formed during these procedures [11].

2. Hydrogen production from biodiesel derived raw glycerol

Currently, almost 95% of global hydrogen production uses raw materials based on fossil fuels, such as CH_4 [15–17]. Given that the global glycerol market currently shows a trend for growth until 2020, an alternative for the large scale use of this product is as raw material for the production of hydrogen and synthesis gas [15,18–20].

The main hydrogen production processes are: water electrolysis [21], and thermochemical [11,16,18,22] and biological processes [23,24]. Among these processes, biological production can be a favorable alternative because it involves less energy expenditure and is carried out at ambient temperature and pressure. When biological reactors are with wastewater, for instance, hydrogen becomes an even more promising alternative energy source [23,24]. The electrolysis of water to produce hydrogen offers advantages such as high purity of the resulting H_2 and absence of waste generated during the process. However, water electrolysis is used only in special cases that require high purity hydrogen, and is not an economically viable alternative source for hydrocarbon substitution. The route most widely used to produce H_2 is the thermochemical process, and CH_4 steam reforming is the most common one [21]. Several hydrogen production technologies using glycerol in the thermochemical route have been studied, but they require power (endothermic reactions) for the conversion of glycerol into synthesis gas. The main processes are steam reforming (SR), autothermal reforming (ATR), supercritical water reforming (SCWR), partial oxidation reforming (POR), liquid phase reforming (LPR) and gasification [11,18,22,25,26].

The hydrogen produced worldwide has many applications. As world faces unprecedented energy challenges, the hydrogen emerges like a promising fuel to move vehicles and to provide power and heat for industries. Despite its employment as energy source, hydrogen can be used as byproduct in chemical industry to obtain cyclohexane, formic acid, hydrochloric acid, polyurethane, methacrylates and also methanol and ammonia that are used to synthetize other important solvents and reagents like formaldehyde, acetic acid, methyl *terc*-butyl ether and urea. Other two process that depend of hydrogen are hydrocracking process carried out in petrochemical refineries and hydrogenation in food industries.

Envisioning a medium term future in which the worldwide use of hydrogen is more widespread and diversified, an important production strategy is decentralization, which will facilitate distribution logistics, reduce costs and increase safety during transportation. In this regard, given that a large proportion of biodiesel plants (glycerol producers) are located in rural regions, hydrogen production from glycerol could become attractive particularly because so many agribusinesses that use hydrogen are established in those very regions. A good example are the agroindustrial plants that operate in the food industry and use hydrogen as feedstock in the production of hydrogenated products such as margarine, hydrogenated fats, etc. Depending on their distance from the hydrogen producers, which are usually located in large cities, the purchase cost of hydrogen for these agroindustrial plants is high. In fact, it should be noted that the cost of hydrogen transportation may account for up to 50% of the price paid by agroindustrial plants. Therefore, the lower cost of hydrogen resulting from shorter transport distances and from the use of glycerol as a renewable raw material can be an advantage for agroindustrial plants located far away from urban centers, thus increasing their competitiveness. The flow chart in Fig. 1 summarizes the raw materials, processes, products and actors involved in the production of hydrogen from glycerol in rural regions.

3. Hydrogen production processes from glycerol

This paper presents an overview of the glycerol reforming processes discussed in recent literature, which include the processes of SR, ATR, LPR, POR, and SCWR [15,25,27,28]. Table 1 describes the main reactions that occur in these processes.

The major constituents of the compounds formed in the thermal decomposition of glycerol are carbon monoxide, hydrogen and

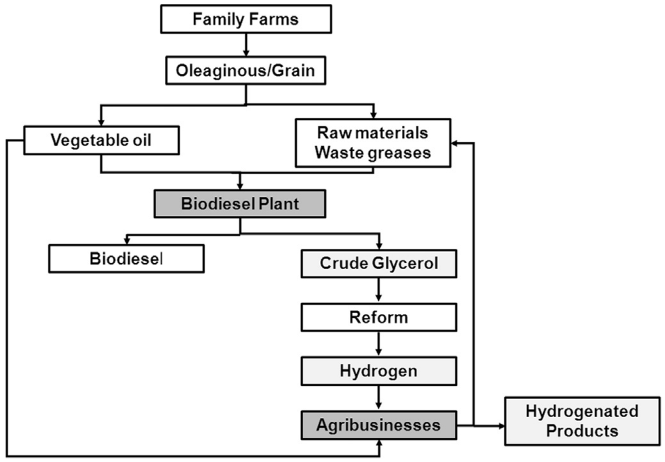

Fig. 1. Example of the interaction between biodiesel plants and agribusinesses with hydrogen.

carbon dioxide. The gaseous mixture resulting from this process also contains small proportions of compounds such as methane and short chain alcohols such as methanol, ethanol [11], ethylene, acetaldehyde, acetic acid, acetone, acrolein, ethanol and water [29,30]. The main glycerol reforming processes involve fixed bed reactors [11], among which glycerol steam reforming has been the most widely studied. Reforming processes usually involve the use of catalysts at temperatures in the range of 300–900 °C [18,31]. Glycerol reforming processes are a promising alternative for hydrogen production, since glycerol is a co-product of the production of biodiesel obtained from renewable sources [12].

In hydrogen production from reforming reactions, catalysts are essential to lower the activation energy, favoring the kinetics of chemical reactions. For the reaction to be more productive and cost-effective, the catalysts used in reforming processes must be highly active and stable, generate the smallest possible amount of coke, be sintering-resistant [17,32,33], and not facilitate undesirable parallel reactions such as methanation (Eqs. (3) and (4)) or Fischer–Tropsch synthesis [34].

3.1. Steam Reforming (SR)

SR is the method most commonly used by the chemical industry to produce hydrogen from natural gas, and is also a promising alternative for glycerol [15,18]. The SR of glycerol process is regarded as one of the most promising, mainly because its scale would not require many changes in current industrial processes for hydrogen production [35]. In this process, glycerol reacts with water vapor in the presence of a catalyst, producing mainly hydrogen, carbon dioxide and carbon monoxide [19,36]. It is most preferred process because hydrogen is simultaneously removed from water, which increases the yield of the reaction.

The global reaction of glycerol steam reforming is represented by Eq. (1), where it can be seen that hydrogen production from glycerol is potentially attractive, considering that the ratio of hydrogen-to-glycerol molecule is 7:1 [16]. Eq. (2) is known as the Water–gas shift reaction, which leads to the production of extra hydrogen. The first reaction is highly endothermic, while the second releases a small amount of energy, but the overall SR process is endothermic [15]. The high consumption of energy for vaporization of the reaction mixture reduces the energy efficiency of the process. However, a large amount of water is necessary to facilitate the gasification of carbon, preventing its deposition in the form of coke on the catalyst. The molar ratios commonly used in studies are glycerol-to-water ratios of 1/9 [37] and 1/6 [16,37,38].

Table 1
Main reactions involved in reforming processes.

Type of reaction	ΔH^0_{298} (kJ/mol)	Nomenclature	Reference
$C_3H_8O_3+3H_2O \leftrightarrow 3CO_2+7H_2$ (1)	+128	Global reaction	[15,16,19]
$CO+H_2O \leftrightarrow CO_2+H_2$ (2)	−41	Water–gas shift	[9,15]
$CO+3H_2 \leftrightarrow CH_4+H_2O$ (3)	−206	Methanation	[15,18,19]
$CO_2+4H_2 \leftrightarrow CH_4+2H_2O$ (4)	−165	Methanation	[9,19]
$H_2+CO \leftrightarrow C+H_2O$ (5)	−131	Coke formation	[9, 12]
$CH_4 \leftrightarrow 2H_2+C$ (6)	+75	Coke formation	[12,18,19]
$2\ CO \leftrightarrow CO_2+C$ (7)	−172	Coke formation	[12,19]
$C_3H_80+0.5\ O_2 \leftrightarrow 2CO_2+4H_2$ (8)	−32	Glycerol oxidation	[9]
$C_3H_8O_3+O_2 \leftrightarrow CO+2CO_2+4\text{-}H_2$ (9)	−315	Glycerol oxidation	[9]
$C_3H_8O_3+1.5\ O_2 \leftrightarrow 3CO_2+4H_2$ (10)	−598	Glycerol oxidation	[18]
$C_3H_8O_3+3.5\ O_2 \leftrightarrow 3CO_2+4H_2O$ (11)	−1565	Glycerol oxidation	[18]
$C_3H_8O_3 \leftrightarrow 4H_2+3CO$ (12)	+250	Glycerol decomposition	[12]

According to several studies [15,16,19,35,39], the best results for the glycerol SR process are obtained at temperatures in the range of 525–725 °C. However, the process is difficult to control in this temperature range; moreover, high temperatures increase operating costs, energy consumption, and the cost of material for construction of the reactor. However at lower temperatures, the main products formed are H_2, CO_2 and CH_4, decreasing the selectivity for H_2. The pressure normally used is about 1 atm, but the ideal situation would be to use vacuum pressures, which would allow for lower reaction temperatures, less energy consumption, and reduce sintering of the catalysts. Table 2 describes some SR studies using glycerol.

The feed rate water/glycerol strongly influences the balance of H_2 production (mainly in the yield and selectivity). Whereas Le Chatelier's Principle, in molar ratios water/glycerol higher the equilibrium shifts towards the excess water consumption, thus producing more hydrogen. At ratios above 9 the increase of H_2 yields occurs more slowly, even at higher temperatures. The amount of water used should not be too high due to the excessive vaporization costs. For the choice of the molar ratio water/glycerol must be taken into consideration the catalyst used and operating conditions (especially temperature and pressure) [35].

The parallel reactions that may occur are shown in Eqs. (3) and (4); they are favored at low temperatures and are little affected by pressure variations. The reaction depicted in Eq. (5) is reversible at the temperatures used in the reforming process, and its purpose is to turn carbon monoxide into carbon dioxide. Eqs. (5)–(7) depict the reactions that can be attributed to carbon formation. The carbon that is formed deposits on the catalyst, blocking the active sites and thus deactivating them [40,41].

In the last decade many research has been done regarding the heterogeneous catalysis involved in the SR reaction of glycerol. The metals most investigated so far, used as active species, were Ni, Pt, Co and Ru [35], highlighting the Ni catalysts, which have been extensively studied in recent years [16,36,37,39,42,43]. In these studies it can be seen that the nature of the support affects mainly the stability of the active phase, and to achieve a stable active phase should have strong interactions between the support and the metal, which leads to increased activity and selectivity [35].

The main function of the support is to maintain the specific area of the active compound, and it also plays an important role by promoting higher thermal stability, and can prevent sintering and coking processes. The choice of support must take into account several factors including neutrality, specific surface area, porosity, structure, electronic modification and metal-support interaction. The morphology of the support must also facilitate contact between the reactants and the active phase, and allow easy removal of the products formed [31,44].

Adhikari et al. [19] analyzed thermodynamic equilibrium in hydrogen production by the glycerol SR process, using variable ranges of pressure, temperature, and water/glycerol infeed rates. The equilibrium concentrations of the different compounds were calculated by the Gibbs free energy minimization method applied to steam reforming. Their study revealed that the best conditions for hydrogen production are: temperature above 625 °C, atmospheric pressure, and a water-to-glycerol molar ratio of 9:1. Under these conditions, methane production was minimized and carbon formation was thermodynamically inhibited.

Catalysts suitable for SR are the ones that can cleave the C–C, O–H and C–H bonds; the main catalysts cited in the literature are metals such as Pt, Ni, Ru, Re, Rh, Ir, Co and Pd. The ones that stand out are Ni-based catalysts with various supports and promoters. They are also used in large-scale industrial processes because of their ready availability and low cost. Noble metal catalysts are commonly employed in steam reforming and in liquid phase reforming (LPR) in the laboratory, due to their high activity and lower susceptibility to coke formation than non-noble metals, but they are expensive, which may render their large-scale application unfeasible [18,20,38,39,41,45].

Dou et al. [37] studied the activity of the Ni–Cu–Al catalyst in hydrogen production by glycerol SR in a fixed bed continuous flow reactor under atmospheric pressure and temperatures of 500–600 °C. The catalyst was synthesized by the co-precipitation method with variable pH. The thermodynamic analysis was performed using a non-stoichiometric methodology based on the minimization of Gibbs free energy. The results revealed that with excess water, a large amount of hydrogen is produced while CH_4 and CO formation is almost negligible, but the authors observed coke formation on the catalyst.

Pompeu et al. [46] prepared Pt catalysts on different supports (SiO_2, γ-Al_2O_3, ZrO_2 and $Ce_4Zr1\alpha$) for glycerol SR at temperatures below 450 °C. The catalysts prepared with acid properties showed low activity, with formation of side-products due to dehydration and condensation reactions that led to coking and catalyst deactivation. On the other hand, the support with neutral properties afforded a catalyst with good activity for gaseous products, high selectivity for H_2 and greater stability over time.

3.2. Partial oxidation reforming (POR) and autothermal reforming (ATR)

In POR, the glycerol reaction occurs under atmospheric pressure, with quantities of oxygen below the optimal stoichiometry for complete combustion [18,62,47]. POR is an exothermic process whose efficiency depends directly on controlling the amount of oxygen that enters the mixture [18,63]. The global POR reaction of glycerol can be expressed by Eq. (10). This process has the potential to be energy efficient and also allows for the production of synthesis gas via different added amounts of oxygen [18,47]. Because it involves rapid consumption of oxygen and high temperatures, the reaction causes various parallel reactions. The complete combustion of glycerol is expressed by Eq. (11).

SR (Eq. (1)) and POR (Eqs. (8)–(11)) occur in the ATR process in the same reactor, i.e., the glycerol is supplied with water vapor and oxygen. This process is considered promising in terms of temperature management, and can be characterized by its energy self-sufficiency, in which SR is an endothermic reaction and POR an exothermic one. Thus, the reactor itself supplies the amount of heat required in the reaction, precluding the need for an external power supply. The addition of oxygen in the process increases hydrogen production in the initial stage, favoring glycerol reforming [9,48,49,64,65]. Oxygen provides the necessary heat through the oxidation reaction, which is very valuable from an energy point of view [66].

The stoichiometric coefficients in ATR differ from those of POR due to the inclusion of water vapor in the combustion process, which should increase the production of hydrogen. The main expected advantages are high efficiency and compactness of the hydrogen generator system. This makes it possible to develop small autonomous units for decentralized small-scale production [9].

Wang et al. [64] carried out thermodynamic studies to investigate the autothermal reforming of glycerol. Their results demonstrate that at high temperatures, large amounts of water vapor and small amounts of oxygen are feasible for this process. Temperatures between 625 °C and 725 °C, vapor/glycerol ratios of 9/1 and 12/01, and proportions of oxygen of 0.0 and 0.4 provide better results in hydrogen production. Under such ideal conditions, methanation and carbon formation can be reduced to low levels [64].

Lin [49], who used a fixed bed reactor with a Pd–Ag alloy membrane and $Ni/CeO_2/Al_2O$ catalyst in the ATR process, reported that the conversion of glycerol increased with increasing pressure, but the hydrogen yield decreased in proportion to this increase.

Autothermal partial oxidation of glycerol is also an attractive method to produce synthesis gas, because viscous glycerol with a high boiling point can be converted into synthesis gas in an adiabatic system, resulting in higher H_2 production. The conversion of glycerol into synthesis gas may reduce humanity's dependence on compounds derived from fossil fuels. For example, a biodiesel plant can use synthesis gas derived from glycerol in the synthesis of methanol [18,67], which in turn is used in the biodiesel production process itself.

Coke formation in ATR is lower than in SR [9,64,65]. The deposition of coke is extremely low in oxidative environments, allowing for long periods of operation without deactivation of the catalyst [18]. Studies by Neto [33] show that an increase in the oxygen supply can significantly reduce carbon deposition, because oxygen oxidizes part of the coke as it forms, producing carbon monoxide.

3.3. Aqueous phase reforming (APR)

The glycerol APR process is an attractive approach for the production of fuels and/or hydrogen, being the Dumesic work in 2002 [68] the pioneer in this process. APR is usually performed at high pressures and moderate temperatures (59 atm/270 °C) in a continuous stream, transforming glycerol into aqueous phase without pre-vaporization [18,27,69]. The global APR reaction is given in Eq. (1). First, glycerol is decomposed, as shown in Eq. (12), after which it can be converted into carbon dioxide and hydrogen by the water–gas shift reaction (Eq. (2)). Hydrogen can be consumed by intermediate compounds such as carbon monoxide and hydroxides, and by dehydration reactions [12,18,59].

Glycerol APR involves cleavage of the C–C, C–H, C–O bonds. Cleavage of the C–H bond leads to the formation of the desired products, hydrogen and carbon dioxide. Another product formed by this cleavage is carbon monoxide, which can undergo undesirable reactions such as hydrogenation, leading to the formation of alkanes (especially CH_4) [34,58,70,71]. This is crucial as CO is a known poison for Pt-based fuel-cell catalysts [72].

Table 2

Summary of references on H_2 production using glycerol in reforming processes.

Process	Reactor	Temperature (°C)	$C_3H_8O_3:H_2O$	Spatial velocity (g glycerol/h g cat)	Pressure	Catalyst	Maximum production of H_2 (%)	Maximum conversion of $C_3H_8O_3$ (%)	Reference
Steam reforming	Fixed bed	300, 500, and 700	1:9	NI*	Atmospheric pressure	Ni–Cu–Al	54.3–70.4	100	[37]
Steam reforming	Fixed bed	500–600	1:9	7.7	0.4 MPa	Ni, Pt, Pt–Ni with γ-Al_2O_3 and La_2O_3	90	100	[42]
Steam reforming	Fixed bed	600–700	1:16	3.4–10.0	Atmospheric pressure	Ni/Al_2O_3	76–99	99.7	[36]
Steam reforming * *in situ* CO_2	Fixed bed	400–700	1:3	NI	Atmospheric pressure	Ni/Al_2O_3	80	100	[43]
Steam reforming	Fixed bed	650	1:6	0.04	NI	Ni/MgO, Ni/CeO_2, and Ni/TiO_2	65.64, 53.88 and 62.20	100, 100, and 98.02	[16]
Steam reforming	Fixed bed	500–600	1:3	7.7	0.4 MPa	$ZrO_2/Ni/Al_2O_3$	70	80	[39]
Autothermal partial oxidation	Fixed bed	490–1155	1:3	NI	50 psi	Pt-, $LaMnO_3$-, and Pt/$LaMnO_3$-coated monoliths	25–122	80–60-Pt 97–63-$LaMnO_3$ 97–88-Pt/$LaMnO_3$	[47]
Autothermal reforming	Fixed bed	600–700	80 wt% glycerol and 20 wt% D.I. water	150,000	Atmospheric pressure	BASF Pt and Rh/Pt double-layer monolith	75	100	[48]
Autothermal steam reforming	Fixed bed reactor with membrane	350 and 700	1:9	5	1–5 bar	$Ni/CeO_2/Al_2O_3$	85.26	99.56	[49]
Autothermal reforming	Fixed bed	900–1200	1:3	10^5	Atmospheric pressure	RhCe/γ-Al_2O_3	79	100	[50]
Partial oxidation reforming	Fixed bed	550–650	1:3, 1:6, 1:9	16,000	Atmospheric pressure	$Ni/CeZrO_2/Al_2O_3$	69–67	40–70	[51]
Autothermal reforming	Fixed bed	550–850	1:3	NI	Atmospheric pressure	Pd/Ni/Cu/K	70	100	[52]
Supercritical water reforming	Fixed bed	445–600	1:4	NI	25 MPa	NaOH, Na_2CO_3, KOH, K_2CO_3	52.0～68.9	NI	[53]
Supercritical water reforming	Fixed bed	450–575	1:3	3.15, 6.45 and 10.8	25 MPa	Co/γ-Al_2O_3, Co/La_2O_3, Co/YSZ, Co/α-Al_2O_3 Co/ZrO_2	50–70	87–97	[54]
Supercritical water reforming	Fixed bed	380–500	1:3	NI	25 MPa	Na_2CO_3	60	100	[55]
Supercritical water reforming	Continuous flow	450–575	1:3	NI	250 bar	Inconel 625 reactor	64–70	100	[56]
Liquid phase reforming	Fixed bed	225	1:3	3.6	2.76 MPa	Pt/MgO, Pt/Al_2O_3, Pt/CeO_2, Pt/TiO_2, Pt/SiO_2	56–70	98	[57]
Liquid phase reforming	Fixed bed	250–270	1:3	NI	38–52 atm	Ni, Ni5Cu, Ni10Cu, Ni20Cu	80–90	60	[58]
Liquid phase reforming	Fixed bed	225	1:3	0.10	2.76 MPa	AP Ni, Raney Ni	50–100	100	[59]
Liquid phase reforming	Fixed bed	225	1:3	5	420 psig	3%Pt/C, 3%Pt1%Re/C, 3%Pt3%Re/C	15–57	5–89	[60]
Liquid phase reforming	Fixed bed	300	1:3	8.4	3.2 MPa	Pt, Ni, Co, and Cu supported on: Al_2O_3, SiO_2, activated carbon, MgO, HUSY, and SAPO-11	41–95	2–22	[61]

* NI: No information.

To obtain high selectivity in hydrogen production, the catalyst must actively cleave the C–C bond and facilitate the displacement of carbon monoxide with water vapor to the surface of the metal. However, it must not favor cleavage of the C–O bond or promote rearrangements that enable the formation of acids or acid solutions, which may occur in the dehydration reaction, leading to the formation of alkanes [34,73].

APR offers numerous advantages over the steam reforming method, e.g., i) low operating temperature and high density of the fluid reduce the cost of reactors; ii) greater heat recovery efficiency because the phase is liquid/liquid; and iii) lower energy cost, because APR does not require a steam feed system [74,75].

The main advantage of this process is that it takes place in the liquid phase, unlike other available technologies in which the processes occur in the gas phase, plus the fact that most biomass-based liquids do not vaporize easily [27].

The disadvantages of APR in comparison to steam reforming are its lower selectivity of hydrogen due to low temperature, which enables the formation of alkanes, and the dependence of the yield of the process on the catalyst [69,75].

The major challenge in the development of catalysts for the APR is to guarantee selectivity for the production of H_2 and not for CH_4, once noble metals have high activity and low deposition of carbon, but their cost and availability have inspired efforts to reduce the usage. Ni is an attractive substitute, but is efficient in the production of CO and methanation and very prone to carbon deposition. An interesting alternative may be the development of biometallic catalysts such as Pt–Ni and Cu–Ni [58,72].

3.4. *Supercritical water reforming (SCWR)*

SCWR is an alternative route for hydrogen production from glycerol. It stands out for operating with a high-pressure and low-temperature system, in which the water is at its critical point (374 °C, 218 atm), which provides interesting properties such as low viscosity, high diffusivity and low dielectric constant [53–55].

In recent years, SCWR has attracted increasing interest owing to its high efficiency and selectivity in H_2 production. Because of the unique properties of supercritical water, this process provides higher space-time yields and reduces mass transfer constraints. Moreover, hydrogen is produced under high pressure and can therefore be stored in cylinders, requiring less energy for its compression [56,76].

Compared to LPR, SCWR has a lower dielectric constant and fewer hydrogen bonds. In supercritical reforming, many organic solvents and gases are completely miscible, favoring a reaction environment with a single fluid phase, which is advantageous when compared to the multiphase system [77,78].

The SCWR process is advantageous because the reactivity of water increases at the supercritical point, and the presence of catalyst favors the reaction. Another advantage is that at temperatures above 600 °C and pressures higher than its critical point, water becomes a strong oxidant. As a result, carbon is preferentially oxidized to CO_2 and low concentrations of CO are formed. The hydrogen atoms from water and glycerol form H_2. The product is composed of H_2, CO_2, CH_4 and CO [11,53,55]. Studies of SCWR without the addition of catalysts show that the glycerol conversion is almost complete, making the process of H_2 production competitive [79].

Guo et al. [53] used a continuous flow tubular reactor for the gasification of glycerol in supercritical water, at temperatures varying from 445 to 600 °C, under a pressure of 25 MPa, and a residence time of 3.9 to 9.0 s. Their results indicate that raising the temperature influenced the efficiency of gasification, but increasing the concentration of glycerol reduced the decreased from 88% to 71% at a temperature of 567 °C. Alkaline catalysts (NaOH, Na_2CO_3, KOH and K_2CO_3) were used to improve the yield and accelerate the displacement reaction. The best use of hydrogen was at 526 °C, which yielded conversions of 52.0–68.9%, with 0.1 wt% of NaOH.

Xu et al. [55] also studied the process of glycerin and glycerol gasification in supercritical water in a continuous flow tubular reactor operating at temperatures between 380 and 500 °C, with and without the use of Na_2CO_3 as catalyst. The best catalytic performance in the gasification of glycerin was with the addition of 0.1 wt% of Na_2CO_3. The residence time of 0.98 min at 500 °C and 1 wt% of glycerol solution resulted in a yield of 98% without catalyst. On the other hand, the mole fraction of hydrogen as a gaseous product was 60%.

The disadvantage of the SCWR process, according to a review of studies carried out by Gou et al. [76], is that high hydrogen yields are obtained with reaction temperatures above 600 °C, while low temperatures (lower than 450 °C) favor the formation of CH_4. The need for high temperatures and high pressures makes the SCWR process economically unattractive. Ortiz et al. [80] have shown that in some cases the H_2 concentration at temperatures near 550 °C is high, but the gas flow rate and conversion of glycerol are lower, beyond the amount of carbon being deposited higher, which may be due to an insufficient glycerol decomposition.

4. Conclusions

The following conclusions can be drawn regarding the reforming processes cited in this paper and perspectives about hydrogen production from glycerol:

New catalysts should be developed, and a more in-depth understanding should be gained about the reactions and variables involved in each type of catalytic reforming process of glycerol, in order to favor the production of hydrogen and reduce coking.

The references consulted for this review do not describe studies about the quality of crude glycerol vis-à-vis the products obtained from glycerol reforming processes (purity of hydrogen) or about hydrogen yields. Given that biodiesel is produced from a variety of raw materials (vegetable oil, animal fats, waste frying oil, and others), which may contain undesirable contaminants, the crude glycerol obtained as a biodiesel co-product also contains contaminants from these raw materials as well as from the biodiesel production process itself (such as catalytic wastes, excess alcohol used in transesterification, etc.). Therefore, studies are needed to identify and quantify contaminants in crude glycerol, and to characterize the transformations these contaminants undergo in catalytic reforming, in order to ensure the quality of feedstock for reformers without impairing the service life of catalysts and reactors, resulting in satisfactory hydrogen yields while maintaining their quality.

The hydrogen produced from raw glycerol is a good alternative to absorb the excess of glycerol generated from biodiesel industries. This perspective is even more promising when considered the distribution of hydrogen to remote areas, from a decentralized hydrogen industrial plant, benefiting the nearest industries such as biodiesel and food industries, utility companies and their rural costumers.

The reforming processes highlighted in this study reveal that obtaining H_2 from glycerol is favorable, resulting in high yields and conversions. At low temperatures the APR processes and SCWR are the most interesting, however they require high pressures, resulting in the increase of materials costs used in reaction systems. By the fact that SR is currently the most common process used in the production of H_2 in the world, choosing this route to the glycerol reforming is advantageous due to the ease of adapting equipment already used by the industry. Additionally, the SR is simultaneously possible to produce extra amount of H_2 from water used in excess, which increases the reaction yield. The POR and ATR processes have the advantage of occurring in atmospheric pressure, but require oxygen and higher temperatures to get good results. Although the reforming processes involve high energy costs, the use of a renewable source, low cost and increased availability, as is the case of glycerol, these can become more affordable technologies.

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