

Use of biofuels to produce hydrogen (reformation processes)

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This *tutorial review* deals with the catalytic reformation of ethanol and glycerol to produce hydrogen that can be used as an energy carrier in a fuel cell. Both the worldwide production of ethanol in large amounts to be used as a biofuel and that of glycerol as a by-product in biodiesel manufacture are presented. The catalytic reformation processes of both ethanol and glycerol are contemplated, including thermodynamic and kinetic aspects. Catalysts are analyzed as a function of operation conditions, selectivity and stability.

1. Introduction

The use of fuel cells for the production of electrical energy from chemical energy is envisaged in the medium term both in the transportation sector and in stationary applications. Fuel cells have higher energy conversion efficiency and generate far fewer pollutants when compared to combustion engines. In this context, hydrogen is contemplated as a clean and effective energy carrier for use as a feed source in fuel cell devices, only H₂O being produced in the electrochemical process. Nowadays, hydrogen is mainly produced from reformation processes of fossil fuels as natural gas and oil derivatives, to be used principally in ammonia production and refinery processes.¹ If the use of hydrogen as energy carrier is contemplated, then other processes for its production must be envisaged because of the environmental problems derived from the use of fossil feedstocks. The production of hydrogen by photodecomposition or electrolysis of water can be proposed as a long-term solution, but the use of biomass can also contribute to this finality.

The production of biofuels to be used in combustion engines in the transportation sector has increased because of the energy policies of several countries. Bioethanol and biodiesel, pure or as blends, are already in the distribution grid for automotive purposes. The current operative production of bioethanol and biodiesel uses several different crops and would be a good starting point to propose the utilization of biomass-derived ethanol or glycerol (1,2,3-propanetriol, which is a by-product of biodiesel production) for hydrogen production through reformation processes. Moreover, there is a growing interest in the utilization of other biomass resources which include agricultural residues and lignocellulosic materials. The development of new transformation processes of such feedstocks would provide other routes of bioalcohols production. In this line, glycerol can also be obtained from fermentation of glucose or as a by-product of the industrial conversion of lignocellulose into ethanol.² Moreover, the production of alcohols in a biorefinery in which the exploitation of a combination of biomass resources was integrated would lead to a more profitable employment of the resources. Besides alcohols, other bio-derived energy carriers such as CH₄ may be produced and integrated in the total process of H₂ production.

Taking into account that a mature technology related with reformation processes of hydrocarbons exists, the implementation of processes for reforming other substrates such as alcohols seems highly realistic. In this context, the use of bioethanol and glycerol may constitute an opportunity to

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produce hydrogen from renewable materials in a medium term.²⁻⁴

2. Bioethanol production

Nowadays, the manufacture of bioethanol constitutes the largest amount of biofuel production and is based on polysaccharide fermentation. Mainly, two crops are used worldwide: sugar cane and corn, the largest producers being Brazil in terms of the former and the US in terms of the latter. Ethanol can be considered as one of the new renewable energy sources, and a number of specific government programs have promoted its use in the transportation sector. The best example is Brazil, where subsidies which existed in the early implantation of the program (1970s) have been progressively removed since the 1990s. Now, in Brazil, ethanol is a global energy commodity that is fully competitive with gasoline. The initial motivation in Brazil to promote the use of ethanol as fuel was the reduction of oil importation, but currently a number of social and environmental advantages are claimed to exist. Among them is the contribution to mitigate the greenhouse effect according to the calculations of the CO₂ released in the total cycle (considering the atmospheric CO₂ converted into biomass by the sugar cane and the CO₂ generated in the ethanol production and combustion).⁵

Sugar cane (*Saccharum officinarum*) is a subtropical graminaceous plant which is grown at low cost, principally in the south central region of Brazil from April to November. The harvested sugar cane cannot be stored and is processed within five days of its harvesting. In the processing, the sugar cane is milled with water to extract the sugar juice and separate the fibrous fraction (bagasse). Bagasse is burnt to produce the energy required in the process; in modern mills a positive energetic balance is attained and excess electrical power is generated. The sugar juice is treated for purification before the fermentation step in which yeast is added and CO₂ is generated. The main organism for fermentation is *Saccharomyces cerevisiae*, an ascomycetous yeast which produces, with a yield of 90–95%, two molecules of ethanol and two of CO₂ from each molecule of glucose fermented; that means 0.51 g of ethanol and 0.49 g of CO₂ from each gram of glucose. Minor by-products obtained are glycerol, higher alcohols and acetic, succinic and lactic acids. A calculation of the energy retained in the two ethanol molecules (heat of combustion) compared with that of the original glucose molecule shows that a 97.5% of the energy of glucose is retained in the ethanol. Distillation of the aqueous solution obtained after the fermentation, leads to the azeotropic solution (96 v/v%), which can be dehydrated by absorption. Fig. 1 shows a simplified flow chart of the process. The appropriate treatment of vinasse coming from the distillation or sludge from the sugar juice treatment may provide additional fertilizer for the crops.^{6,7}

Calculations of the energy generation and consumption in the production of ethanol from sugar cane in Brazil showed a renewable output to a fossil input ratio of ca. 8–10.⁵ The renewable/fossil energy balance is not so favourable when the production of ethanol from corn is contemplated, and an average ratio 1.5–1.8 has been calculated depending on the

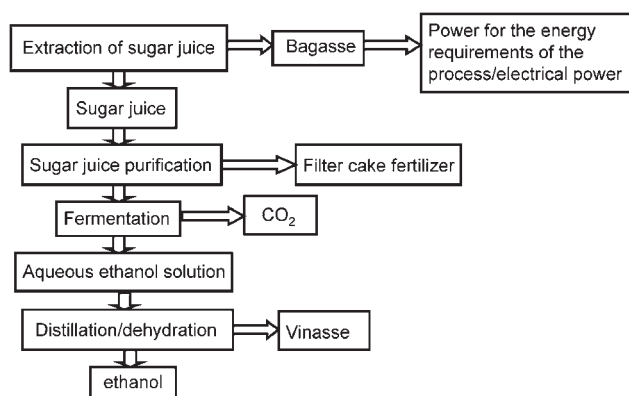


Fig. 1 Flow chart of the ethanol production from sugar cane.

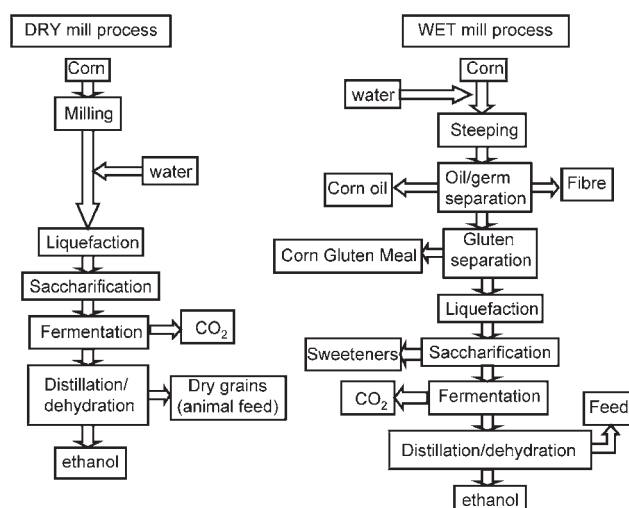


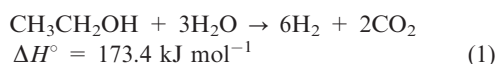
Fig. 2 Flow chart of the ethanol production from corn.

process used for the ethanol production: dry grind or wet milling. However, other valuable products can be obtained from these processes.⁷ The production of ethanol from corn is based on the transformation of the corn starch to glucose and maltose, and then the fermentation of the simple sugars to ethanol. Starch is formed by two polymers of glucose: a linear polymer with α -1–4 bonds (amylose) and a branched polymer (amylopectin) that contains α -1–4 and α -1–6 bonds. The polymeric nature of the starch is broken by the action of enzymes and heat. Two enzymes are used in the industrial process. In the first step, α -amylase hydrolyzes the polymers to shorter chains (dextrins), which remain in solution; this is the liquefaction step. Then, by the action of glucoamylase in the saccharification step, dextrins transform to simple sugars, glucose and maltose (α -1–4 glucose dimer). Although the biological bases for the transformation of corn into ethanol are the same for both the wet milling and the dry grind processes, when the wet milling process is used, valuable co-products such as corn oil, gluten and syrup are obtained. Contrarily, mainly ethanol and animal feeds are produced in the dry grind process.⁷ Simplified schemes for both dry and wet processes are given in Fig. 2.

3. Bioethanol to hydrogen: analysis of the reformation processes

The use of ethanol in reformation processes to produce hydrogen reveals several advantages derived from its renewable, nontoxic, liquid and easy-to-handle nature.

In the steam-reforming process (ESR), besides the extraction of the hydrogen contained in ethanol, it is possible to extract that contained in the water that reacts stoichiometrically with it, as follows:



providing 6 mol of H₂ per mol of ethanol reacted.

In view of the fact that at least three mol of water are necessary for each mol of ethanol to be reformed, if ethanol was produced for use in a reformation process the distillation step should not be completed as it is when using ethanol as fuel in the combustion engines whose production is described above.

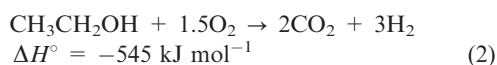
Taking into account that the process is envisaged with an energetic aim, besides the yield of H₂, the energy requirements are of principal importance.

3.1 Thermodynamic considerations

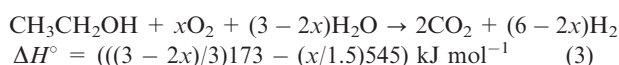
The ethanol steam-reforming reaction is a highly endothermic process that is carried out catalytically. However, energetically, ESR is favoured with respect to steam-reforming of other hydrocarbons which, as stated in the introduction section, are currently used to produce H₂. The comparison of the energy required for the extraction of 1 mol of H₂ from ethanol or from other hydrocarbons such as methane, shows that the former is lower (32.33 kJ in comparison with 72.82 kJ per mol of H₂ produced at 600 K). On the other hand, the H₂ produced/C in the feedstock ratio is lower for ethanol than for methane (3 in comparison with 4).

A comparison of the energy balance of ethanol steam-reforming and its subsequent use in a fuel cell with that of the combustion of ethanol, is favorable to the former (70% higher) if the energy efficiency of hydrogen oxidation in a fuel cell (*ca.* 50%) and that of the combustion process (*ca.* 25%) are taken into consideration.⁸ In this calculation, the energy required to vaporize ethanol and water previously to the reformation or that necessary to distil ethanol useful for combustion engines were not regarded.

If the introduction of O₂ into the steam-reforming reactant mixture is envisaged, a more favoured energetic balance can be achieved because the exothermic catalytic partial oxidation of ethanol can be operative:



The global process:

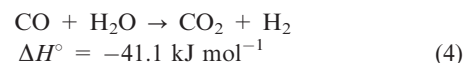


may be adjusted, tuning the ethanol : water : O₂ ratio, considering both the H₂ yield and the energy requirements that decrease with the increase in O₂ introduced.

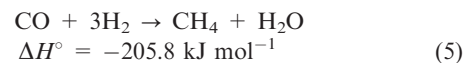
In a combined process, oxidative ethanol steam reforming (OESR), the endothermic reaction may control the temperature of the fast exothermic reactions. This is an advantage for mobile applications and may allow an effective control of the total process, avoiding the need of additional cooling equipment for controlling the temperature of exothermic reactions.

Several thermodynamic analyses of the ESR and OESR as a function of temperature and ethanol : water : O₂ ratio have been done.^{9,10} Theoretically, the ESR process can be accomplished at temperatures higher than 500 K with hydrogen, carbon oxides and methane as major products, and it shows high values of equilibrium constant for temperatures above 600 K.

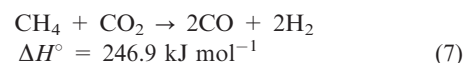
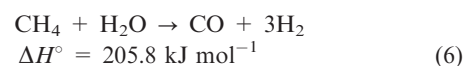
An increase in temperature favours the CO production because the water gas shift (WGS) reaction is slightly exothermic:



Depending on the nature of the catalyst, the methanation reaction can take place to some extent:

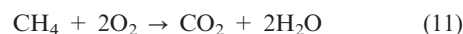


Due to the exothermic nature of this reaction, the production of methane is not favoured at high temperature, but its reformation with steam is. Above 823 K, both the reforming of methane with water (steam-reforming) or/and CO₂ (dry reforming) are thermodynamically feasible:

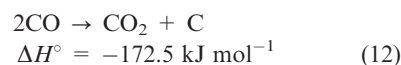


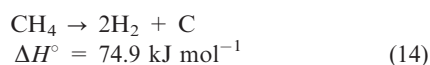
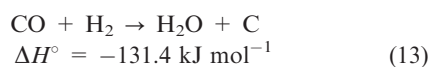
An increase in water in the reactants assists the production of CO₂ and H₂ but the heat provided to carry out the process increases too, because water must be vaporized.

Additional oxidation reactions may take place when oxygen is co-fed in the reactant mixture:



A main problem of the practical use of reformation processes is the formation of coke that causes the deactivation of catalysts. Principally, the following processes contribute to this:





The Boudouard disproportionation (12), and the reverse of carbon gasification with H_2O (13) are the major reactions responsible for the formation of carbon deposits at low temperatures. At temperatures higher than 700 K the carbon formation is mainly due to methane decomposition (14).

The coke formation decreases with the increase in $\text{H}_2\text{O} : \text{EtOH}$ or $\text{O}_2 : \text{EtOH}$ ratios and the contribution of the carbon gasification with water (reverse of reaction (13)) or oxygen (15) may take place:



A main challenge in the practical use of ethanol to produce hydrogen is the development of a simple process which combines a favourable energetic balance and the production of H_2 with an appropriate purity to be fed into the fuel cell. Depending on the type of fuel cell used, and the composition of the reformed effluent, the effluent must be purified. Molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) operate at high temperature and may transform CH_4 or CO impurities in the anode chamber. Contrarily, polymer electrolyte membrane fuel cells (PEMFC) and phosphoric acid fuel cells (PAFC) do not allow CO concentrations higher than 50 ppm and 0.05%, respectively. An integrated system in which the reformed effluent is purified can be proposed on the basis of well-known technologies for high purity hydrogen production, including WGS (4), catalytic selective oxidation (10), methanation (5) and/or use of H_2 selective membranes.¹

3.2 Catalytic steam-reforming of ethanol

Several metallic active phases have been used for the catalytic steam-reforming of ethanol; mainly nickel, cobalt and noble metals such as rhodium, palladium, ruthenium, platinum and iridium. All these metals are capable of producing C–C scission, which is an indispensable function for this reaction.³

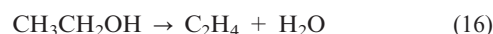
A number of surface science studies of ethanol interaction with different transition metal surfaces have been published,¹¹ and the knowledge of the fundamental mechanistic aspects of the evolution of surface species can well illustrate the mechanisms which would participate in the ethanol reforming processes.

Ethanol interacts with the metallic surface and an ethoxide species is formed. On platinum group metals (Ni, Pd and Pt) the ethoxide species can lead to an aldehyde intermediate carbon- and oxygen-bonded ($\eta^2(\text{C},\text{O})$) or oxygen-bonded ($\eta^1(\text{O})$), the latter configuration being promoted on surfaces precovered with oxygen and facilitating the desorption of acetaldehyde. The $\eta^2(\text{C},\text{O})$ configuration leads to an acyl intermediate which may evolve to CO and CH_4 . The surface composition and crystallographic structure determine the mechanism of surface acyl decomposition, and the rate determining step may be the C–C or the C–H scission. If ketene is formed after dehydrogenation of surface acyl species, an ulterior rapid C–C scission takes place. On the other hand, over Rh surfaces $-\text{CH}_2\text{CH}_2\text{O}-$ oxametallacycle species are proposed to be formed after ethanol interaction and the

desorption of acetaldehyde is not favoured. Over unreduced samples, adsorbed acetaldehyde is mainly observed.¹²

Besides the active phase, the support, if it exists, can also interact with ethanol and produce its transformation, thus influencing the reaction selectivity. Moreover, the support may promote water splitting and favour OH migration. Ethanol steam-reforming has been studied over several pure oxides that can be used as supports.¹³ Over ZnO , CeO_2 , and La_2O_3 the reformation of ethanol occurs in some extension.

Acid centres on the support produce the dehydration of ethanol to ethylene:



which may polymerize and be a precursor of carbon deposits. This is the case of $\gamma\text{-Al}_2\text{O}_3$ which has been widely used as a support in the preparation of catalysts for the steam-reforming of ethanol, where the addition of alkaline additives which neutralize the acid centres has been shown to be effective in the decrease in ethylene selectivity for these catalysts.

On the other hand, oxides having basic centres may lead to acetaldehyde formation which may evolve through an aldol condensation reaction to higher oxygenates production; in this context the formation of dimethyl ketone has been shown to be favoured over ZnO under steam-reforming conditions and high contact times:



It has been suggested that the surface oxygen and OH mobilities on the support play an important role in the reformation processes. CeO_2 and $\text{CeO}_2\text{-ZrO}_2$ have been used as support in numerous studies of ESR and OESR. The promoter effect of CeO_2 is related with the ability of (i) acting as an oxygen storage material in oxidation reactions, (ii) dispersing active noble metal phases inhibiting their sintering, (iii) promoting WGS, (iv) facilitating the coke gasification. Addition of ZrO_2 to CeO_2 enhances the ceria activity for oxidation reactions because of the increase in oxygen mobility.¹⁴ The increase in the activity of $\text{Rh/CeO}_2\text{-ZrO}_2$ catalysts on ESR has been related with the increase in OH mobility at the catalyst surface.¹⁵

A pH controlled hydrothermal synthesis of Y_2O_3 allowed to prepare supported nickel catalysts with similar nickel dispersion but different crystal size of Y_2O_3 . Samples with higher Y_2O_3 surface area showed higher activity in the OESR, this was related with the surface oxygen mobility on Y_2O_3 .¹⁶

The temperature range 573–1073 K used in the ethanol reformation processes is wide and the working temperature highly determines the selectivity to several products. Usually, under the operating conditions utilised, products other than CO_2 and H_2 are obtained because other reactions are operative. At low temperature and/or under ethanol conversion values lower than 100%, acetaldehyde is usually found. This is because either the dehydrogenative oxidation of ethanol (8) or the dehydrogenation of ethanol is favoured depending on the presence or not of O_2 in the reactant mixture:



The ESR has been proposed to proceed over different systems following a first step of ethanol dehydrogenation to acetaldehyde (18), which decomposes into CO and CH_4 :



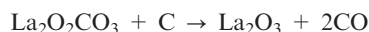
The use of high temperature can produce the reformation of CH_4 (6). The ulterior WGS reaction (4) will control the distribution of products. The WGS could be promoted at low temperatures by several metallic functions or oxide supports, under these conditions giving low selectivities to CO.

A major consideration in the OESR is the O_2 : EtOH ratio: an excess of O_2 besides the reduction of the hydrogen yield may produce the oxidation of the metallic particles, leading to oxidic phases that behave poorly in the reformation.

In what follows, the behaviour of catalytic systems on the ethanol reformation processes will be discussed in separate sections devoted to nickel-, cobalt- and noble metal-based catalysts.

Nickel-based catalysts. ESR and OESR have been extensively studied over catalysts containing nickel as active phase, because nickel-based catalysts are largely used in industry for the reformation of hydrocarbons. Ni is known to be capable of cleaving the C–C bond effectively, to participate in the water gas shift reaction for converting CO into CO_2 (4) and to produce the reformation of CH_4 (reactions (6) and (7)).

Several promoters and supports have been used to inhibit the formation of carbon deposits, which is the main cause of deactivation of the above-mentioned nickel-based catalysts. A positive effect on the stability of Ni/SiO₂ catalysts under OESR conditions was found when copper was added. This was related to the alloying of nickel with Cu, which inhibits the formation of a metal carbide, which is considered an intermediate in the filamentary carbon growth. Temperatures around 973 K and $\text{H}_2\text{O} : \text{EtOH} : \text{O}_2 = 1.6 : 1 : 0.5$ ratios are proposed for the operation of these catalysts.¹⁷ The addition of potassium to Ni/MgAl₂O₄ catalysts lowers the rate of carbon formation and prolongs the lifetime of the catalysts under ESR conditions, and this has been related with a better steam adsorption in the K-doped catalysts. Other promoters such as Ag produce a more rapid deactivation of Ni/MgAl₂O₄ catalysts. It has been proposed that the Ni step-sites that are the most active ones in reforming are blocked by Ag. In this case, the higher ethanol concentration on the surface may be the agent responsible for the faster carbon formation.⁸ As regards the support, La₂O₃ was shown to lead to a very stable Ni/La₂O₃ catalyst in which the formation of carbon deposits are inhibited under ESR conditions.¹⁸ In this case, the presence of LaO_x decorating the nickel particles is proposed to react with CO₂ and produce La₂O₂CO₃ that reacts with surface carbon following:



The use of alkali-metal doped Ni/MgO led to active and selective catalysts, and these were proposed as suitable for hydrogen production to be fed into MCFC. The Ni sintering under reaction conditions is inhibited, alkali addition stabilizes the system, and the rate of coke formation is very low when compared with nickel catalysts on acidic carriers. This positive effect may be related with an electronic enrichment of the active phase induced by the alkali-metal addition, which is reflected by depression of both the Boudouard reaction (12), and of hydrocarbon decomposition.¹⁹

Studies of OESR over Ni–Rh/CeO₂ catalysts indicated that the crystallite size of CeO₂ influences their catalytic performance.²⁰ Catalysts prepared with nanocrystalline CeO₂ (crystallite size around 6.5 nm) showed a high rhodium dispersion, strong Rh–CeO₂ interaction, and synergistic Ni–Rh interaction giving a highly dispersed Ni–Rh redox couple that shows high catalytic activity for ethanol conversion and high selectivity to H₂ at relatively low temperatures (around 723 K).

Cobalt-based catalysts. Cobalt-based catalysts have been proposed as an alternative to the use of nickel-based catalysts in the ESR because of their low working temperature and low generation of by-products.³

Studies of ESR over catalysts derived from Co₃O₄ or Co_{3–x}Fe_xO₄ followed by X-ray diffraction under *operando* conditions or by *in situ* magnetic measurements have allowed to determine the evolution of oxidic phases and the performance of the solids as a function of the temperature used.²¹ The initial oxides produce the dehydrogenation of ethanol to acetaldehyde (18), and transform progressively to CoO and metallic cobalt, the presence of Co aggregates is related with the activation of the solids on the ESR. The presence of Fe modifies the reduction properties of the cobalt and consequently the catalyst activation and the catalytic behaviour. The addition of small amounts of iron enhances the catalytic performance of the solids decreasing the production of by-products such as CO or CH₄.

Supported cobalt catalysts on a variety of oxides have been studied on the ESR. Besides the action of the oxide support, which depends on its acidic/basic and redox properties and follows the general trends exposed above, the interaction of cobalt phases with the support determines the reducibility of cobalt species and consequently their performance in the process.³ In this context, the interaction between the cobalt phases and support may depend on the preparation method used. This aspect was evidenced in Co/CeO₂ catalysts, where the Co₃O₄/CeO₂ precursor prepared by impregnation resulted in a more difficult reduction than the Co₃O₄/CeO₂ prepared by co-precipitation, the latter being more active in ESR.²²

Co/ZnO catalysts were demonstrated to have a good performance in ethanol and acetaldehyde steam reforming: 5.5 H₂ mol/ethanol mol reacted were obtained at 623 K when bioethanol-like mixtures EtOH : H₂O = 1 : 4 (v/v) were reformed; only a low amount of methane was detected as by-product.³ A DRIFT-mass spectrometry study under reaction conditions showed that the reaction takes place *via* the initial dehydrogenation of ethanol to acetaldehyde; ethoxide, acyl and acetate species are present under ESR. On fresh Co/ZnO catalyst, surface acetate species are formed after acetaldehyde adsorption and produce H₂ and CO₂ under steam-reforming conditions. Co/ZnO catalyst deactivates during ESR by formation of carbon deposits, and over deactivated catalyst the acetaldehyde decomposition (19) is favoured with respect to its reformation.²³



The addition of Na promoter to Co/ZnO catalysts inhibits the carbon formation under ESR conditions and enhances the stability of the catalysts.³

Recently, bimetallic cobalt-based catalysts with noble metals (Rh, Ru) have been shown to be highly performing

systems in the OESR; a periodical regeneration by coke burning has been proposed.²⁴

Noble metal-based catalysts. Rh-, Pt-, Ru-, Pd- and Ir-based catalysts have been studied on the ESR and OESR reactions. Due to the usually low content of the noble metal active phase in the catalysts, the characteristics of the support, mainly related with its acidic–base properties and the interaction with the supported noble metal, have been evidenced to be of main relevance. Principally Al₂O₃-supported and CeO₂-based-supported catalysts have been studied.

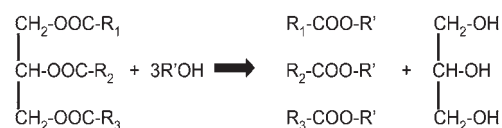
Among noble metals, Rh-based catalysts have been the most studied because of their better performance in the process. The use of high temperatures and an excess of water has been proposed to be used in the ESR over Rh/Al₂O₃ for decreasing the carbon deposition. At 923 K ethylene produced by dehydration of ethanol (16) over the support is rapidly reformed, and acetaldehyde, which is produced by ethanol dehydrogenation (18), decomposes to CO and CH₄ (19), which is subsequently reformed (6). The addition of small amounts of O₂ to the reactant mixture (0.4% v/v) decreases the catalyst deactivation by carbon deposition but promotes the metal sintering, probably because of the local increase in temperature.²⁵ Mg–Al-based spinels deposited on alumina beds have been proposed to modify the acidic properties of Al₂O₃ and to improve the stability of rhodium particles upon reaction.²⁶ A number of studies of ESR over Rh/CeO₂–ZrO₂ (Ce : Zr = 4–1 : 1) have been carried out at lower temperatures (673–773 K). High activity and selectivity were reported.¹³ The addition of small amounts of K to Rh/CeO₂–ZrO₂ system produced a beneficial effect on catalyst stability. Activation with O₂ at 473 K has been proposed to eliminate the carbonaceous deposits.²⁷

The modification of Al₂O₃ by Ce led to a more active Pt/CeO₂–Al₂O₃ catalyst, and the strong interaction of Pt and CeO₂ has been proposed to be responsible for the behaviour of the catalyst; this interaction may affect the adsorption decomposition of ethanol to CH₄ and its reforming (6).²⁸

In the case of Ir/CeO₂ catalysts, the stability on OESR has also been related with a strong interaction between Ir and CeO₂. This interaction would be the fact responsible for the presence of highly dispersed Ir particles and would prevent their sintering. Moreover, the high oxygen storage-release capacity of CeO₂ contributes to the resistance of the catalyst to deactivation by coke deposition.²⁹

4. Biodiesel production and glycerol generation

Biodiesel is a renewable fuel which is usually produced from vegetable oils such as soy, sunflower, peanut, corn or palm, but there is an increased interest in the use of other alternative crops unsuitable for food that could grow on degraded or marginal land (e.g. *Jatropha curcas*). Moreover, biodiesel can also be produced from animal-based fats and used (recycled) domestic or industrial oils and greases. The European Union produced around 90% of the world's biodiesel in 2005. Biodiesel production in the United States has steadily increased from 2005 and is expected to reach 2 billion gallons by 2009. Other countries such as Brazil, India and China could follow upward tendencies in biodiesel use. In this context, a



Scheme 1 Transesterification of triglycerides with alcohol, R'OH (R' = CH₃ if methanol is used).

high increase in biodiesel production is expected in a short time.³⁰

Nowadays, biodiesel is mainly produced through the catalytic transesterification reaction of triglycerides with an appropriate alcohol. Although different alcohols can be used, methanol is currently preferred. Besides the corresponding methyl esters, glycerol (1,2,3-propanetriol) forms as by-product in a ratio of 1 mol glycerol : 3 mol ester (Scheme 1).

Despite the fact that the chemical nature of biodiesel differs from that of the petroleum-derived diesel fraction, the behaviour in Diesel engines is quite analogous. Thus, biodiesel can be blended or directly used as an alternative bio-fuel for Diesel engines. The use of biodiesel shows a number of environmental advantages with respect to petroleum-based diesel fuel; biodiesel has low amounts of sulfur-content compounds and about 50% reduction of CO₂ emission when compared to petroleum-based diesel fuel.

Fig. 3 shows a general flow chart of the biodiesel production using the methanol transesterification of triglycerides. Glycerol (by-product) usually represents ca. 10 wt% of the products obtained and must be removed to allow the use of the esters as suitable products of diesel-type fuel.

Presently, glycerol is used in multiple areas ranging from cosmetics and pharmaceuticals to explosives. However, as a result of the increased production, a surplus of glycerol is expected in the world market in the short term. A saturated market for glycerol could occur in the conventional areas of use; in fact, the price has already dropped in the last 5 years.

The crude glycerol generated during biodiesel production is a by-product for which environmental and financial aspects must be taken into account. The initial glycerol aqueous solution contains excess of alcohol, and some soap and inorganic salts, coming principally from the alkaline hydroxide catalyst used in the transesterification step. In this form, the by-product glycerol has low value and disposal is considered hazardous. Additional refining of crude glycerol must be done when sold to cosmetics

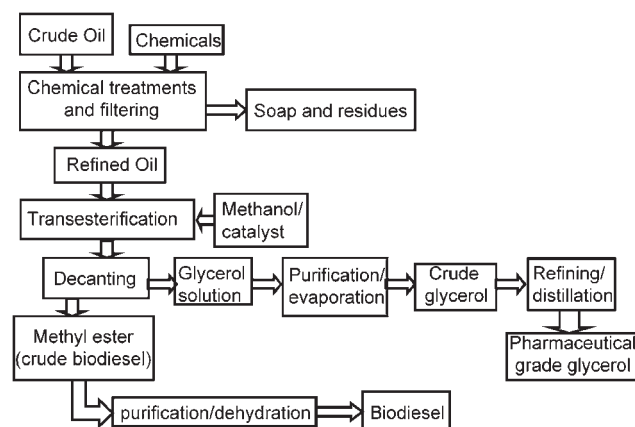
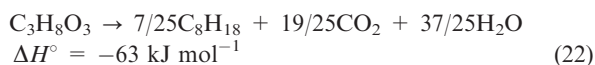
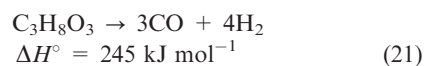


Fig. 3 Simplified diagram of biodiesel production using the methanol transesterification process.

and pharmaceutical sectors, and this is a major energetic issue. One option for glycerol use in the energetic sector is simply burning it to obtain electric energy from conventional systems. When burned to produce thermal energy, the theoretical heating value of glycerol is 1570 kJ mol⁻¹. At the current price, this gives a heating value which is slightly less than the current value of natural gas. However, the presence of water in the crude glycerol decreases its heating value, and the salts, unless removed, create a significant amount of ash and solid residues.

New explorations for uses of glycerol appear to be of increasing interest. Several reviews have recently been published dealing with the selective transformation of glycerol into commercially available valued products.³¹ Moreover, the conversion of glycerol into a CO and H₂ mixture (syngas-type) (21) and then its conversion to liquid fuels (*i.e.* hydrocarbons or methanol) through the exothermic Fischer–Tropsch synthesis has recently been analyzed.² The combination of both processes results in an exothermic process (22) when *n*-octane is considered.



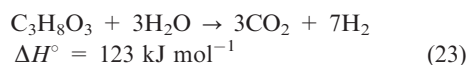
The glycerol conversion into gas mixtures of H₂ and CO is effective over platinum-based catalysts at temperatures from 498 to 620 K. Pt–Ru and Pt–Re alloys have been proposed to be suitable bimetallic catalysts.²

Glycerol can be alternatively envisaged as a hydrogen-carrier; the use of catalytic glycerol reforming processes can be applied to extract hydrogen. In this sense, biodiesel would be fully integrated in the renewable fuel concept through its own use as biofuel, and that of the H₂ obtained from the glycerol by-product, as clean fuel for fuel cell devices. However, we recall that the biodiesel available at present cannot be considered a 100% biomass-derived fuel because of the use of petroleum-derived methanol currently used in the process.

In what follows we will present the current developments achieved in the hydrogen production using glycerol reformation processes.

5. Glycerol reformation

Hydrogen can be generated from glycerol by means of reforming processes, in both the liquid and the gas phase. The neat reaction of glycerol reformation with water is:



To occur effectively, this reaction must be catalyzed. So far, both commercial catalysts and newly developed catalysts have been used. However, significant improvements in both the catalysts and the process still need to be made.

5.1 Aqueous phase reformation

Despite the fact that the process of aqueous phase reformation (APR) of glycerol must be run under pressure, the APR

presents some advantages: (i) low-grade purity glycerol can be fed, (ii) the process occurs at low temperatures (< 573 K) in a single reactor, (iii) hydrogen can be extracted and purified from the product stream (CO₂ and H₂) using well-known pressure swing adsorption technology.

The reaction conditions prevent steam formation and ensure that the catalytic process takes place in the aqueous phase. The process implies the breakdown of the C–C, C–H and O–H bonds of the glycerol molecule, preserving the C–O bonds. In fact, on the metal surface the dehydrogenation of the glycerol molecule to adsorbed intermediates occurs and then their evolution to H₂ and CO involves the C–C scission. Further, CO gives CO₂ through the WGS reaction (4). However, under the reaction conditions, the hydrogenation of CO and/or CO₂ to hydrocarbons may occur. An efficient catalyst for hydrogen production from APR of glycerol must avoid the C–O cleavage and the CO or CO₂ hydrogenation to alkanes which are highly favoured under the reaction conditions. Small amounts of methane and ethane are usually found in the gas phase. The resulting liquid phase is a complex mixture of glycerol derivatives such as C1–C3 alcohols and C2–C3 acids, among others. Thus, a major challenge for APR of glycerol is the maintenance of a high selectivity to hydrogen, avoiding parallel or consecutive hydrogen-consuming reactions, *i.e.* methanation (5) or Fischer–Tropsch reactions. However, even though high yields of hydrogen can be achieved in the gas phase the processing of the resulting highly diluted aqueous solutions containing a complex mixture of by-products may be very difficult and expensive. Nevertheless, currently Virent's BioForming process is based on APR to produce hydrogen from sugar-derived feedstock.³²

Pioneering work concerning reformation of glycerol and other biomass-derived polyalcohols in aqueous phase has been reported by Dumesic's group and a very complete overview has been published.³³ Different active catalysts with the previously indicated catalytic functions which are necessary for the reaction, include metals of groups 8, 9 and 10.

Monometallic, supported catalysts based on Ni, Pd, Pt, Ru, Rh and Ir have been studied for this process, the most useful being Pt- and Pd-based catalysts. The effect of the support has also been analyzed. Varying from silica to alumina, Pt catalysts improve activity and selectivity for hydrogen production while keeping low alkane production. A 3 wt% Pt/Al₂O₃ catalyst produced hydrogen with a selectivity up to 75% at 498 K and 51% at 538 K from a 1% glycerol aqueous solution in a single reactor. The activity of Pt catalyst can be further improved by adding a second metal.

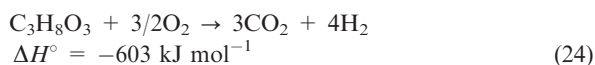
Bimetallic, Ni-, Pd- and Pt-based catalysts have been studied in depth in the APR process. It has been suggested that alloying Pt with Ni, Co or Fe improves the activity for H₂ production by electronic modification, which causes a decrease in the heats of CO and H₂ adsorption, thereby increasing the fraction of the surface atoms available for reaction with the polyalcohol.³³

For Pd-based catalysts, the rate limiting step for APR appears to be the WGS reaction (4), and the addition of a promoter for the WGS reaction accounts for the improvement of catalytic behaviour.

Ni-based catalysts are active for APR but they produce significant amounts of alkane and are not stable under

reaction conditions. However, the selectivity of Ni-based catalysts has been improved by adding Sn. Moreover the stability of the systems increases when a bulk catalyst is used.³⁴ Raney-Ni-Sn catalysts with Ni : Sn atomic ratios of up to 14 : 1 exhibited hydrogen selectivity comparable to that of the 3 wt% Pt/Al₂O₃ catalyst. The effect of Sn addition on Ni-catalysts is related with the diminution of the rate of the methane formation while maintaining high rates of C–C cleavage. This system has been reported as quite stable for more than 250 h of reaction.³³

APR of glycerol and, by extension, of polyols, can be a choice for producing hydrogen because the low temperature used favours the WGS reaction, decreasing the content of CO in the gas effluent. However, from the energetic point of view, the endothermic APR of glycerol could be improved by coupling the catalytic partial oxidation reaction (24) to achieve an overall autothermal process.



This possibility and the use of aqueous phase oxidation with hydrogen peroxide have recently been analyzed from a thermodynamic point of view.³⁵

5.2 Gas phase reformation

Production of hydrogen from glycerol has also been attempted in the gas phase by steam-reforming (GSR). So far very few reports have been published, but recently interest has increased, and several thermodynamic analyses of the process have been reported.³⁶ The advantage of this approach is that the reforming reaction can be performed using well-known technology, conducted at atmospheric pressure and using conventional fixed-bed reactors. Steam-reforming of mixtures of crude glycerol (55%) and methyl esters of fatty acids from a biodiesel plant was first reported over a commercial Ni catalyst (Süd-Chemie) by Chornet and co-workers using a fluidized-bed reactor.³⁷ The experiments at 1123 K with a 2–3 steam to carbon molar ratio (S/C) produced up to 76% of the theoretical hydrogen attainable from the feedstock. Although the performance of the process did not decrease significantly during the on-stream time analyzed, a gradual increase of methane in the gas phase was noticed. It was already suggested that a further WGS reaction (4) would be needed for a total CO conversion and achievement of higher yields in hydrogen. These interesting preliminary results already pointed out the necessity of minimizing the coke formation and of taking into account the presence of the inorganic impurities in the crude glycerol feedstock for a long-term catalyst performance.

In 2005, Suzuki and co-workers communicated the development of a novel efficient catalyst for glycerol steam-reforming in the gas phase.³⁸ A Ru-based catalyst afforded very high activity in a prolonged run (24 h) at 873 K and in addition, a small amount of carbon was deposited on the spent catalyst. They studied group 8, 9 and 10 metals supported on a variety of oxides: Y₂O₃, ZrO₂, CeO₂, La₂O₃, SiO₂, MgO and Al₂O₃. The catalytic tests were performed over reduced catalysts in a fixed-bed reactor, operating at atmospheric pressure and a temperature range of 773–873 K. Using an aqueous

solution of special grade glycerol and a S/C = 3.3, a 3 wt% Ru/Y₂O₃ catalyst yielded up to 80–90% of hydrogen. A small amount of methane was determined as by-product but the selectivity to CO was over 20%. The activity order determined from these experiments (Ru ≈ Rh > Ni > Ir > Co > Pt > Pd > Fe) is comparable to that measured for the steam reforming of methane. A high selectivity to CO₂ was common for catalysts containing basic supports. Ru/Al₂O₃ was a poor catalyst for glycerol reformation to hydrogen and gave high selectivity to CH₄ and low selectivity to CO₂. Ru on the basic MgO showed very low conversion of glycerol; this behaviour is parallel to that shown in the CH₄ reforming with CO₂ (7). The ruthenium oxide on MgO is hard to reduce and the number of active centres would decrease in this case. Ru/Y₂O₃ and Ru/ZrO₂ were the best performing systems.

Very recently, Fernando and co-workers have reported extensive thermodynamic analysis and experimental studies of GSR.³⁶ The number of moles of hydrogen produced has been calculated on the basis of minimising the Gibbs free energy. High temperatures, low pressures and high water-to-glycerol molar ratios favour the hydrogen production. The behaviour of GSR system is very similar to that of ESR. Above 900 K, at 1 atmosphere of pressure and with a water : glycerol ratio = 9 : 1, the methane production is minimized and carbon formation is thermodynamically inhibited. An upper limit of 6 was determined for the moles of hydrogen produced per mol of glycerol, vs. the stoichiometric limit of 7.

GSR was studied over MgO-, CeO₂- and TiO₂-supported nickel catalysts. Ni/MgO was found to be the highest performing catalyst under the experimental conditions investigated (water : glycerol molar ratio = 6 : 1, *T* = 823–923 K). A maximum H₂ yield of 4 mol of H₂ per mol of glycerol was reported. On the other hand, a comparison of the catalytic behaviour on GSR of Ni and noble metals (Pd, Pt, Ru, Rh) supported on ceramic foam monoliths (92% Al₂O₃ and 8% SiO₂) has been done.³⁶ The glycerol conversion at 1123 K was in the order: Ni > Ir > Pd > Rh > Pt > Ru. Whereas the H₂ selectivity was in the order: Ni > Ir > Ru > Pt > Rh, Pd. Ni-based catalysts reached a glycerol conversion of 82% and a selectivity to H₂ of 60% at 1123 K with a water : glycerol molar ratio = 6 : 1. Monoliths used as support were modified with CeO₂ because of the oxygen storage-release capability of this material and its resistance to coke deposition; the resulting catalysts showed higher H₂ selectivity. Notably, low CH₄ production was achieved when operating at low feed flow ratio (0.15 ml min⁻¹, GHSV = 15300 h⁻¹) and 1123 K; methane steam reforming (6) could then take place. However, high CO selectivity is obtained and H₂/CO mixtures from 1.6 to 2.0 are produced.

Autothermal gas phase reforming of reagent grade glycerol to synthesis gas has been reported over noble metal catalysts using appropriate adjustment of feedstock/air and feedstock/steam ratios. For such purposes, specially designed reactors able to operate under short contact times (*ca.* 10 ms) and with alumina foams-supported Pt and Rh catalysts have been developed by Schmidt and co-workers.⁴ A 5 wt% Rh system with ceria supported on an Al₂O₃ washcoat layer exhibits good performance with selectivity to by-products (methane, ethane, ethylene and acetaldehyde) less than 2% at *T* = 1073–1373 K, yielding H₂ : CO ratios of = 3.9–0.9 : 1.

A non-reduced multicomponent catalyst containing Ni, Cu and Pd on a K-treated γ -alumina was used for the GSR and autothermal steam reforming of glycerol. Using a S/C = 3 and an oxygen-to-carbon molar ratio (O/C) in the feedstock of 0.3, the main problem of char deposition is minimized. At 1123 K a hydrogen yield of ca. 60% is achieved over this material.³⁹

Our laboratory has recently initiated the study of the oxidative steam reforming of glycerol over bimetallic cobalt-based catalysts that exhibit high performance in the reformation of bioethanol. The preliminary results indicate that reagent grade glycerol-ethanol mixtures containing up to 15 wt% of glycerol can be efficiently reformed at temperatures as low as 648 K in a gas mixture that only contains H₂, CO₂ and CH₄.

Concluding remarks

The demand of hydrogen to be fed in fuel cells can increase in a short term. Currently, hydrogen is mainly available from fossil-derivative sources using well-known reforming technology. Oil depletion and environmental concerns are exerting pressure to search for new renewable sources. The use of bio-derived feedstocks can contribute to achieve this objective.

Bio-derived ethanol and glycerol are produced worldwide in increasing amounts due to the increased use of biofuels. The current reformation technologies may allow to obtain hydrogen from these biofuels. However, efforts are required in relation to both catalytic and technological aspects.

ESR and OESR are feasible but the formulation of new improved catalysts, which are more stable and selective, is desirable to run the process energetically compatible with the fuel cell use.

Gas phase reformation of glycerol has only been recently explored and appropriate catalysts must still be developed. The reformation of glycerol and other bio-derived polyols has been afforded in aqueous phase; a challenge being the feasibility of selective reforming of concentrated glycerol solutions at low temperatures.

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