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Avanços na reforma autotérmica do etanol para produção de gás hidrogênio: uma revisão

Advances in ethanol autothermal reform for hydrogen gas production: a review

Avances en la reforma autotérmica de etanol para la producción de gas hidrógeno: una revisión

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Resumo

A preocupação com o aquecimento global e o alto consumo de combustíveis fósseis levou alguns países a buscar e investir em novas fontes de energia que sejam eficientes e menos poluentes. Entre essas alternativas, as células a combustível de hidrogênio são uma solução potencial que pode gerar energia limpa. Devido a produção industrial de hidrogênio ser realizada pela reforma a vapor do metano, que utiliza matéria-prima não renovável e é endotérmica (resultando em altos custos de energia), a reforma autotérmica do etanol vem se apresentando como uma tecnologia interessante, pois combina uma matéria-prima renovável com as reações de reforma (endotérmica) e oxidação parcial (exotérmica), conseguindo assim a auto-suficiência energética no processo de conversão de etanol em hidrogênio. Apesar dos vários estudos referentes a reforma autotérmica do etanol, para nosso conhecimento nenhum artigo apresentou uma revisão detalhada dos principais avanços realizados nos últimos anos para esse processo. Assim, esta revisão apresenta os principais resultados para a reforma autotérmica do etanol, nos últimos anos, em três áreas principais: Catalisadores, Projeto de Reatores e Modelagem / Simulação. Este trabalho identificou que os maiores avanços foram feitos no desenvolvimento de novos catalisadores e no projeto de reatores, enquanto a área de modelagem/simulação ainda possui poucos estudos para descrever com eficiência a termodinâmica da reforma autotérmica do etanol.

Palavras-chave: Reforma autotérmica de etanol, catalisadores, projeto de reatores, modelagem e simulação.

Abstract

Concern about global warming and the high consumption of fossil fuels has led some countries to seek and invest in new energy sources that are efficient and less polluting. Among these alternatives, hydrogen fuel cells are a potential solution that can generate clean energy. Due to the industrial production of hydrogen being carried out by steam reforming of methane, which uses non-renewable raw material and is endothermic (resulting in high energy costs), the autothermal reform of ethanol has been presenting itself as an interesting technology, as it combines a renewable raw material with the reactions of reform (endothermic) and partial oxidation (exothermic), thus achieving energy self-sufficiency in the process of converting ethanol to hydrogen. Despite the various studies referring to the autothermal reform of ethanol, to our knowledge, no article has presented a detailed review of the main advances made in recent years for this process. Thus, this review presents the main results for the autothermal reform of ethanol, in recent years, in three main areas: Catalysts, Reactor Design and Modeling / Simulation. This work identified that the greatest advances have been made in the development of new catalysts and the design of reactors, while the modeling/simulation area still has few studies to efficiently describe the thermodynamics of the autothermal reform of ethanol.

Keywords: Autothermal reform of ethanol, catalysts, reactor design, modeling and simulation.

Resumen

La preocupación por el calentamiento global y el alto consumo de combustibles fósiles ha llevado a algunos países a buscar e invertir en nuevas fuentes de energía que sean eficientes y menos contaminantes. Entre estas alternativas, las celdas de combustible de hidrógeno son una solución potencial que puede generar energía limpia. Debido a que la producción industrial de hidrógeno se lleva a cabo mediante la reforma de vapor de metano, que utiliza materia prima no renovable y es endotérmica (lo que resulta en altos costos de energía), la reforma autotérmica de etanol se ha presentado como una tecnología interesante, ya que combina una materia prima renovable con las reacciones de reforma (endotérmica) y oxidación parcial (exotérmica), logrando así la autosuficiencia energética en el proceso de conversión de etanol en hidrógeno. A pesar de los diversos estudios sobre la reforma autotérmica del etanol, hasta donde sabemos, ningún artículo ha presentado una revisión detallada de los principales avances realizados en los últimos años para este proceso. Por lo tanto, esta revisión presenta los principales resultados para la reforma autotérmica del etanol, en los últimos años, en tres áreas principales: catalizadores, diseño de reactores y modelado / simulación. Este trabajo identificó que se han realizado los mayores avances en el desarrollo de nuevos catalizadores y en el diseño de reactores, mientras que el área de modelado / simulación todavía tiene pocos estudios para describir eficientemente la termodinámica de la reforma autotérmica de etanol.

Palabras clave: Reforma autotérmica de etanol, catalizadores, diseño de reactores, modelado y simulación.

1. Introduction

The Global socioeconomic activities are currently linked to energy consumption. Driven by economic, industrial and population growth this consumption has been increasing (Sáez-Martínez, Lefebvre, Hernández, & Clark, 2016). The high demand for energy is met by an energy matrix composed of more than 87% of fossil fuels, such as oil, natural gas and mineral coal (Abokyi, Appiah-Konadu, Abokyi, & Oteng-Abayie, 2019), for having high energy density, easy transportation and storage in addition to other economical features (Sinigaglia, Freitag, Kreimeier, & Martins, 2019).

Intense consumption of these resources has generated pollution and in the last 50 years the concentration of carbon dioxide in the atmosphere has increased by 30%, reducing air quality (Herbert & Krishnan, 2016). The concentration of gases that cause the greenhouse effect reached 407 ppm in 2017, this being the highest value of the last 800 thousand years, in addition to the global temperature having increased by 1.1 °C in comparison to the pre-industrial period (Zhou et al., 2018). The rise in global temperature directly affects the climate of different regions of the planet, increasing the incidence of environmental disasters that can harm natural and human systems, causing deaths and losses in the economy (Zhou et al., 2018; Smith et al., 2014; Fischer, Shah, Tubiello, & Van Velhuizen, 2005; Parry, Rosenzweig, Iglesias, Livermore, & Fischer, 2004). In view of the growth in energy demand and the need to avoid polluting energy sources, unconventional energy sources have been researched together with technologies for greater use of energy. These new technologies are one of the keys to avoid an energy crisis in the future and reduce air pollution (Đozić & Urošević, 2019; Baruah, Dixit, Basarkar, Parikh, & Bhargav, 2015).

Hydrogen gas is a clean and efficient fuel and it is becoming increasingly significant in the world energy economy (Vita, Pino, Italiano, & Palella, 2019). It is estimated that 96% of hydrogen gas production is made from fossil fuels, such as natural gas, the main technology being steam reforming of natural gas (Vita et al., 2019; Fahim, Al-Sahhaf, & Elkilani, 2012). The hydrocarbon steam reform consists of the reaction between water vapor and the raw material inside tubular reactors filled with catalysts, in order to allow the breakdown of hydrocarbon molecules, releasing the hydrogen gas that is obtained with high purity from of some purification process (Baruah et al., 2015; Vita e al., 2019; Iulianelli, Dalena, & Basile, 2019; Vlãdan, Isopencu, Jinescu, & Mares, 2011; Song, 2002). Generally, this purification is carried out by adsorbent vessels that allow the passage of hydrogen while retaining the by-products of the reform reaction. However, the hydrocarbon steam reform consists in endothermic reactions, requiring a large amount of external energy for the reactor, in addition to consuming a non-renewable raw material. Equations 1, 2 and 3 demonstrate the reform of different types of hydrocarbons (Baruah et al., 2015; Vita e al., 2019; Fahim et al., 2012; Muritala, Guban, Roeb, & Sattler, 2019).

$$C_n H_m + nH_2O \leftrightarrow nCO + \frac{(m+2n)}{2} H_2, \quad \Delta H > 0 \tag{1}$$

$$C_n H_m O_p + (n-p)H_2O \leftrightarrow nCO + (\frac{m}{2} + n - p)H_2, \quad \Delta H > 0 \tag{2}$$

$$C_n H_m O_p + (2n-p)H_2O \leftrightarrow nCO + (\frac{m}{2} + 2n - p)H_2, \quad \Delta H > 0 \tag{3}$$

While the reforming reactions are endothermic, in the partial oxidation reactions the reaction of raw material occurs with an amount of oxygen less than necessary for complete combustion. As it is an oxidation reaction, it is evident that its main advantage is to release energy and for this reason, partial oxidation reactions have been extensively studied in recent years. Equation 4 demonstrates the partial oxidation of a light hydrocarbon (Muritala et al., 2019; Elbadawi et al., 2019; Nourbakhsh, Shahrouzi, Ebrahimi, Zamaniyan, & Nasr, 2019; Nahar & Dupont, 2014; Hartmann, Maier, Minh, & Deutschmann, 2010; Jin, Rui, Tian, Lin, & Li, 2016; Afolabi & Kechagiopoulos, 2019).

$$C_n H_m + \frac{n}{2} O_2 \rightarrow nCO + \frac{m}{2} H_2, \quad \Delta H > 0 \tag{4}$$

The ethanol autothermal reform presents itself as an alternative process in the substitution of hydrocarbons from non-renewable sources and has attracted the attention of researchers for the promising results presented by allowing the reduction of energy expenditure of the reform reaction. In the autothermal reform, renewable raw material ethanol is used and, in the process, there may be oxidation of part of this raw material, releasing energy used in the reform reaction and thus producing hydrogen gas without depending on an external energy source for the reactor. The ethanol autothermal reform is presented in Equation 5 (Vita et al., 2019; Liu, Lin, Man, & Ren, 2019; Cormos, 2014, Chen et al., 2009; Shekhawat, Spivey, & Berry, 2011).

$$C_2H_5OH + xO_2 + (3-2x)H_2O \leftrightarrow (6-2x)H_2 + 2CO_2 \tag{5}$$

Several renewable fuels are being studied to produce hydrogen gas, but among them, ethanol has gained greater interest from researchers, due to its various production routes, being easy to store, transport and without toxicity, in addition to contributing to the reduction of carbon dioxide emissions into the atmosphere (Baruah et al., 2015; Vita et al., 2019; Xuan, Leung M, Leung D, & Ni, 2009; Giwa, 2013; Almeida, 2010; Holladay, Hu, King, & Wang, 2009; Xue et al., 2018).

In recent years, it is possible to notice a greater number of researches regarding the steam reform of ethanol in relation to its autothermal reform. This is due to the fact that the catalysts of the autothermal reform, by non-noble metals, still do not promote high conversion of the raw material or when they succeed, they do not remain stable for long periods. Therefore, the most recent studies on this process have focused on the development of new catalysts, new reactor configurations and few studies to better understand the process in the area of modeling and simulation, in order to obtain high ethanol conversions at temperatures lower process (Baruah et al., 2015; Cormos, 2014).

Due to the advantages that the ethanol autothermal reform has in relation to the steam reform of hydrocarbons, the objective of this work is to review the main advances obtained in relation to the autothermal reform of ethanol, and session 2 will deal with research on new catalysts, session 3 will address the main advances in the construction of reactors and finally, session 4 will present studies on modeling and simulation.

2. Catalysts for ethanol autothermal reforming

Catalysts in the ethanol autothermal reform are extremely important for high reactions by attenuated reaction, in addition to preventing the formation of coke that is deposited on the catalysts impairing the reaction performance (Baruah et al., 2015; Vita et al., 2019; Holladay, Hu, King, & Wang, 2009). There are countless equations that represent the real process of autothermal reforming since the reaction path depends on each catalyst with each catalyst promoting a unique reaction path, so the catalyst must be chosen carefully. For this work, the autothermal reform is represented by equation 5. Among the most used catalysts are noble metals, non-noble metals and bimetallic, described, briefly, in subtopics 2.1; 2.2 and 2.3. (Baruah et al., 2015; Vita et al., 2019; Jin, Rui, Tian, Lin, & Li, 2010; Cai et al., 2008).

Despite the catalytic quality of noble metals, they represent a high cost to chemical processes. Thus, there is a great effort by researchers in the synthesis of efficient catalyst with non-noble metals, in order to make the processes economically viable.

2.1. Noble metal catalysts

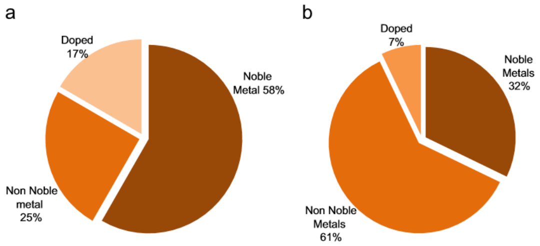
These catalysts are composed of noble metals, such as rhodium, palladium, platinum, ruthenium and iridium. The most used technique for the synthesis of noble metal catalysts is capillary impregnation, which consists of dissolving the noble metals in an aqueous organic solution for impregnating supports and sequentially calcining to remove impurities (Baruah et al., 2015). Chen et al. (2009) synthesized an iridium based catalyst supported on lanthanum obtaining high conversion, selectivity and stability for the catalyst in the operational conditions of the autothermal reform of ethanol. Another study evaluated the relationship between the structure of the catalyst and its performance in the ethanol autothermal reform (Cai et al., 2008). It has been demonstrated that the dispersion of iridium in the catalytic support (CeO2), the basicity of the support surface and structural defects in it are key elements in the activity and selectivity of the catalyst, as well as in its resistance to aging. Rhodium, platinum, palladium and ruthenium have also been extensively studied on different supports, reaching even 100% conversion of ethanol in its autothermal reform with high hydrogen selectivity (Baruah et al., 2015; Divins, López, Rodríguez, Vega, & Llorca, 2013; Tosti et al., 2013; Hung, Chen, Liao, Chen, & Wang, 2012; Santucci et al., 2011).

There is no doubt about the efficiency that noble metals such as rhodium, platinum, palladium, and ruthenium have in the autothermal reform of ethanol since they reach 100% of conversion, are stable and selective. But the high cost involved in using it has shifted the focus of researches to development of non-noble metals. This is primarily because of the adversely impact market acceptability of noble metals.

2.2. Non-noble metal catalysts

They are synthesized in a similar way to noble metal catalysts. In addition to non-noble metals being cheaper compared to noble metals, the literature has shown that most catalysts based on non-noble metals have a crystalline structure which can make it very stable without losing catalytic activity (Baruah et al., 2015). Due to the high activity of these catalysts and their lower cost in relation to those of noble metals, it can be seen from Figure 1 that, as of 2009, research with non-noble metals grew and exceeded the number of research with noble metals.

Figure 1 - Trends in catalyst studies for ethanol autothermal reform



a) Until 2009, b) 2009-2014

Source: Modified from Baruah et al. (2015)

Figure 1 informs that since 2009 the focus of research in relation to catalysts for the autothermal reform of ethanol has shifted from noble to non-noble metal catalysts. This was due to the high cost involved in noble metals. In addition, tests performed with non-noble metals and the combination of these and noble metals, suggest that these new catalysts have high efficiency, stability and selectivity, which can reduce costs and maintain catalytic quality in the autothermal reform of ethanol.

Among the non-noble metals studied, nickel and cobalt stand out with good stability and selectivity for the ethanol autothermal reforming, in addition to contributing to the non-formation of coke during reactions (Baruah et al., 2015; Xue et al., 2018; Hung et al., 2012; Greluk, Rybak, S Lowik, Rotko, & Machocki, 2015; de Lima et al., 2012; Furtado, Alonso, Cantao, & Fernandes-Machado, 2011; Chen et al., 2010; da Silva, da Costa, Souza, Mattos, & Noronha, 2010; Huang, Xie, Chen, Chu, & Hsu, 2010). Greluk et al. (2015) synthesized a cobalt-based catalyst on a zirconium support. The results indicated that for an oxygen / ethanol molar ratio of 0.9 and a vapor / ethanol molar ratio of 9 it is possible to inhibit the formation of coke in the conversion of ethanol to hydrogen gas. However, it was observed that the presence of oxygen in the reaction can oxidize the cobalt particles, decreasing the activity of the catalyst and requiring higher temperatures to achieve a complete conversion of ethanol. Hung et al. (2012) studied the reaction pathways of the ethanol autothermal reforming in different catalysts. Authors concluded that the breakdown of the ethanol molecule occurs preferentially when using catalysts based on copper, nickel, palladium and platinum. It was observed that high molar ratios of steam/ethanol and oxygen/ethanol increased the performance of the studied catalysts, enabling adequate ethanol conversions.

Huang et al. (2010) and Furtado et al. (2011) synthesized nickel-based catalysts for the ethanol autothermal reforming. The results showed that it was possible to obtain a conversion of 100% of ethanol, and the catalyst remained stable in the 30-hour tests. It was also demonstrated that the presence of oxygen inhibited the formation of coke in the catalysts in relation to the process of ethanol reforming (without oxygen) reducing the deactivation of the catalyst due to the non-formation of coke. Xue et al. (2018) synthesized a nickel catalyst with the addition of lanthanum in a CeO_2 support. The results indicated that lanthanum increased the catalytic surface area and left the nickel more stable and dispersed in the support. In addition, it facilitated the transport of oxygen within the pores of the catalyst and it was possible to achieve a conversion of 100% of ethanol, in addition to a molar composition, on a dry basis, of 69.3% of H_2, having been the ethanol autothermal reforming reaction conducted at 600 °C. However, the catalyst showed greater stability at a temperature of 550 °C.

2.3. Bimetallic catalysts

These catalysts consist of the impregnation of non-precious metals (such as nickel and sodium) in catalysts based on noble metals. The most studied bimetallic systems were the nickel, palladium and silver ternary and the platinum, ruthenium and sodium ternary (Baruah et al., 2015; Lin, Liu, & Chang, 2010; Wang et al., 2011). Lin et al. (2010) found a conversion of 80% of ethanol in the use of the ternary catalyst of nickel, palladium and silver, at temperatures below 420 °C while Wang et al. (2011) achieved a conversion of 100% to ethanol with the ternary catalyst of platinum, ruthenium and sodium, for a temperature of 350 °C, and at 400 °C the conversion of ethanol dropped to 95%. Martinelli, Watson and Jacobs (2019) investigated the addition of sodium in a platinum-based catalyst. The authors concluded that the addition of sodium decreased the activity of the catalyst, but increased its selectivity in hydrogen production, with no carbon monoxide being found even at temperatures below 300 °C. Based on these studies, it was realized that the addition of non-noble metals in the noble metal catalysts can improve the conversion of ethanol to hydrogen gas, reduce the formation of coke and carbon monoxide, allowing lower temperature values for the process of autothermal reforming of ethanol (Baruah et al., 2015; Martinelli et al., 2019). Although it differs from the definition of bimetallic catalysts (mixture of noble and non-noble metals), researchers synthesized a catalyst based on barium, strontium, cobalt and iron in a perovskite support (CaTiO3) and carried out the ethanol autothermal reforming in a membrane type reactor. The results indicated a production of 3.5 mol H_2 / mol ethanol at a temperature of 750 °C, and the catalyst remained stable during the period of 180 hours and allowed a good permeability for the oxygen present in the reaction (Jin et al., 2016).

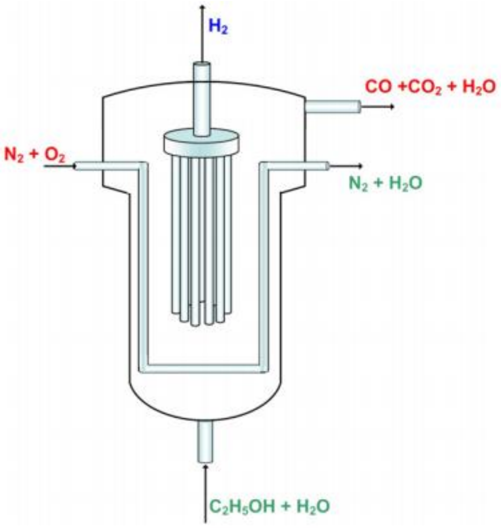
Thus, we observed that the combination of noble and non-noble metals produces efficient and cheaper catalysts, which can achieve conversions of 100% of ethanol. In addition to high conversion, these catalysts are selective to H_2, stable at high temperature, permeable to the oxygen present in the reaction, and can also reduce the formation of coke and CO during the autothermal reform of ethanol.

3. Reactors for ethanol autothermal reforming

The literature, in addition to research on catalysts for the ethanol autothermal reforming has works in relation to the development of catalysts that can improve this process, including creating patents for new reactor configurations (Baruah et al., 2015; Galluci, Annaland, & Kuipers, 2010).

Galluci et al., (2010) studied, based on a phenomenological model, the production of high purity hydrogen in a fluid bed membrane reactor. The results of the simulations showed that in the reactor configuration studied at high pressure and temperature, it is possible to obtain high conversion of ethanol and the recovery of 100% of the hydrogen produced. The reactor scheme modeled is represented in Figure 2.

Figure 2 - Schematic representation of the fluidized bed membrane reactor for the ethanol autothermal reform

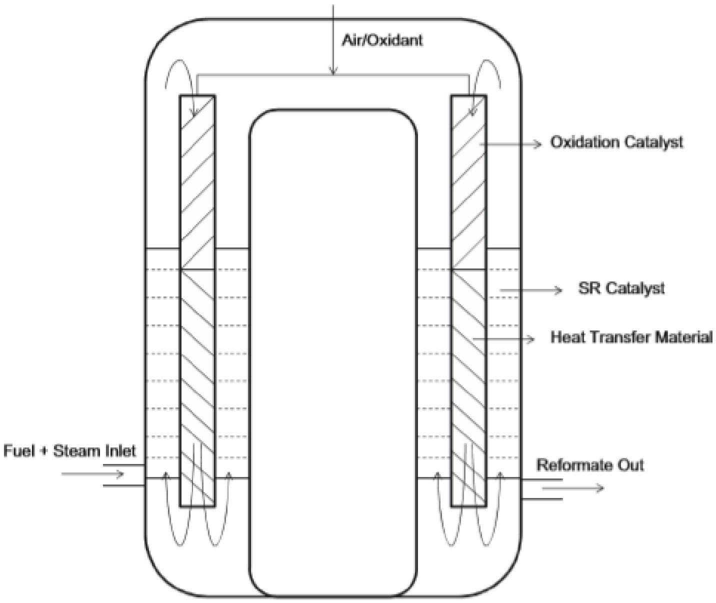


Source: Galluci et al., (2010)

Figure 2 illustrates that steam and ethanol enter the reactor where the catalyst is mildly fluidized. The reactor contains an ultra-pure Pd-based membrane that can recover, theoretically, 100% of hydrogen.

In order to make better use of the heat released by the partial oxidation of ethanol in its steam reforming, a patent was developed for a cylindrical annular reactor capable of forming a quadruple tubular structure, represented in the Figure 3 (Yamazaki, Maruko, & Komori, 2011).

Figure 3 - Schematic representation of the annular reactor for the autothermal reform



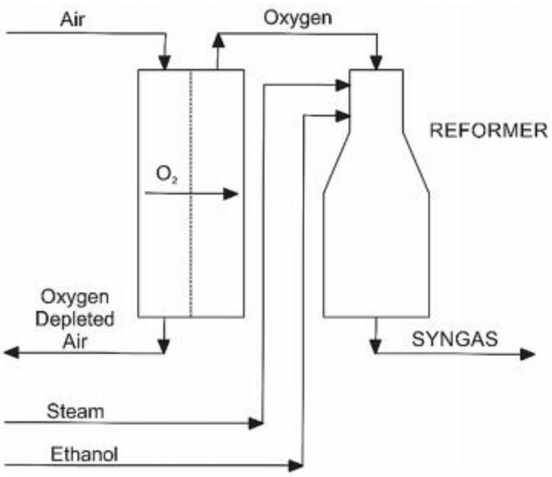
Source: Modified from Yamazaki et al. (2011)

For the reactor in Figure 3, the partial oxidation of the fuel occurs inside the inner tubes and the heat released in the reaction is conducted to the outer tube, where the reforming of the raw material occurs.

One study involved both the synthesis of a catalyst based on barium, cobalt, strontium and iron, in addition to a high-density ceramic membrane reactor. It was possible to obtain an adequate oxygen flow to the reaction medium and both the catalysts and the reactor membrane remained stable during the autothermal reforming of ethanol. In addition, hydrogen production in the experiment was satisfactory, demonstrating the potential of the catalyst and reactor configuration for the autothermal reforming of ethanol (Jin et al., 2016).

The oxygen used in the ethanol autothermal reforming is first separated from the air and then goes to the reactor. This separation process increases the cost of the autothermal reforming process and in view of this scenario, Fischer and Iribarren (2017), in Aspen Plus, proposed a countercurrent arrangement for air and water vapor, capable of separating oxygen from atmospheric air more economically. Under conditions optimized for the proposed configuration and for the autothermal reforming process, it was possible to reduce the annual cost in relation to the conventional process by 72.2%. The traditional configuration of oxygen separation from air is represented in Figure 4.

Figure 4 - Traditional configuration of the oxygen-air separation system in the autothermal reform



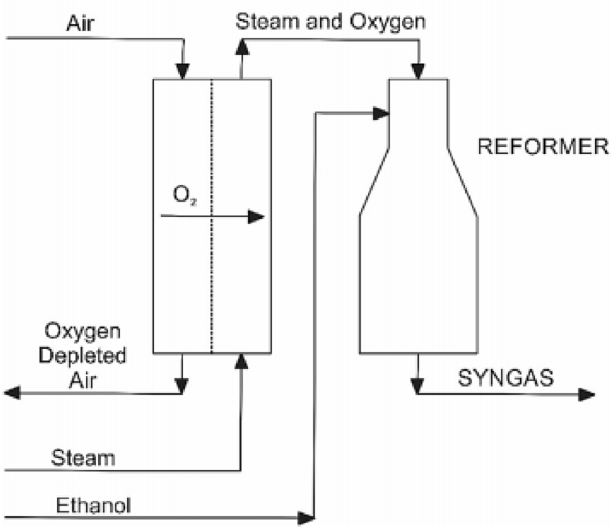
Source: Modified from Fischer and Iribarren (2017)

We can observe, by Figure 4, that in traditional configuration the oxygen is first separated from the air and then injected into reactor with other reagents. Due to the cost of this system, Fischer and Iribarren (2017) proposed a new configuration shown in Figure 5.

Figure 5 shows that the new oxygen separation system occurs in conter-current with steam. The authors concluded that in this new system oxygen separation occurs faster and cheaper than the traditional way.

Membrane reactors call scientists' attention to the autothermal reforming of ethanol, as they offer the opportunity to produce hydrogen gas and separate it from the other reaction products in a single step, without the need for a purification process (Iulianelli & Basile, 2019; Iulianelli, Ribeirinha, Mendes, & Basile, 2014; Yun, Lim, & Oyama, 2012). The use of these membrane reactors for the production of hydrogen gas began to be studied in the 1960s, as it brings some operational advantages. Due to the fact that the membrane reactor is not a closed system, it allows a production greater than the thermodynamic limit to be reached, since during the reaction there is a constant withdrawal of the product formed, favoring the reaction towards the products (Iulianelli et al., 2014).

Figure 5 - New configuration proposed to separate oxygen from air in the autothermal reform



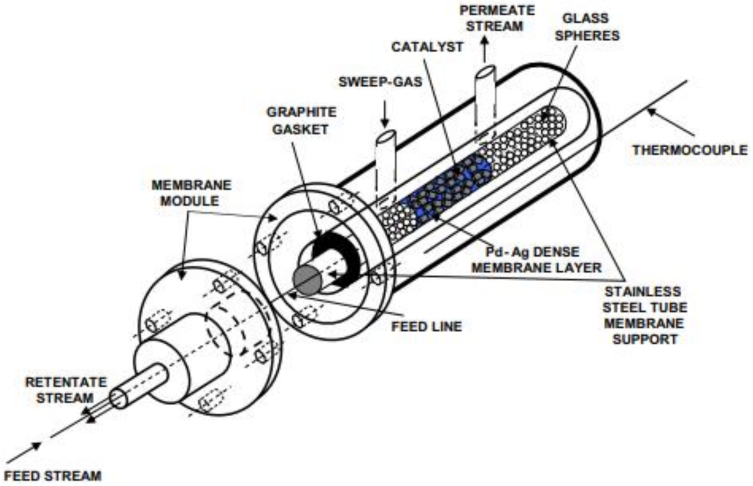
Source: Modified from Fischer and Iribarren (2017)

The operating cost can also be reduced, as the membrane reactor eliminates the hydrogen purification step, reducing the scale of the industrial plant, saving on materials and employees, in addition to allowing for softer operating conditions (lower temperatures) (Iulianelli et al., 2014; Yun et al., 2012).

Among the various inorganic membranes studied, the membrane made of palladium supported on metals or ceramics has been preferred by scholars, as they have high mechanical resistance and allow a high flow of hydrogen gas (Iulianelli et al., 2014; Basile et al., 2008). In general, palladium membranes proved to be superior to other materials because they have greater permeability for hydrogen gas and more recent studies try to improve the performance and resistance of these membranes to the poisoning of gaseous by-products from the addition of other metals, such as copper, silver, gold, nickel, among others (Iulianelli et al., 2014; Yun et al., 2012; Ballesteros, Daza, Valdés, Ratkovich, & Reyes, 2019). Figure 6 shows a traditional tubular reactor scheme filled with a catalyst and a membrane.

Figure 6 illustrates the permeate stream at the end of the reactor. The specific permeability of the membrane for a product can reduce the scale of the plant and even eliminate the purification stage.

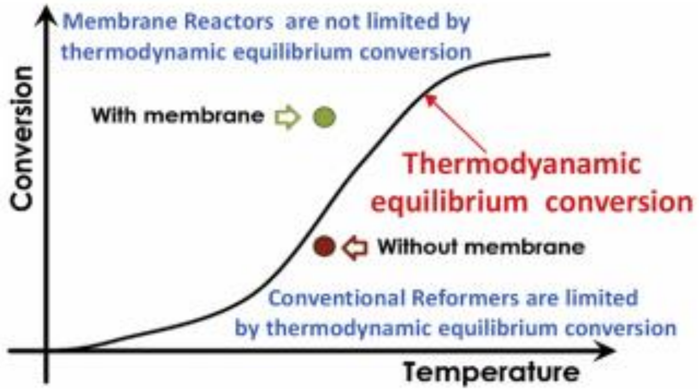
Figure 6 - Schematic representation of a membrane reactor for the ethanol autothermal reform



Source: Modified from Iulianelli; Dalena and Basile (2019)

From the schematic representation of this reactor that despite having an inorganic membrane, it is very similar to a traditional fixed bed tubular reactor. The possibility of exceeding the thermodynamic limit of the reaction conducted in traditional reactors in membrane reactors is illustrated in Figure 7.

Figure 7 – A comparative between conversion obtained in a membrane reactor and traditional reactor



Source: Modified by Iulianelli, Dalena and Basile (2019)

Figure 7 shows a curve that represents the thermodinamic equilibrium conversion limit for chemical reactions. For traditional reactors, this limit cannot be exceeded. Whereas in the membrane reactors this limit can be overcome. This occurs because during the reaction there is a constant output current with the product.

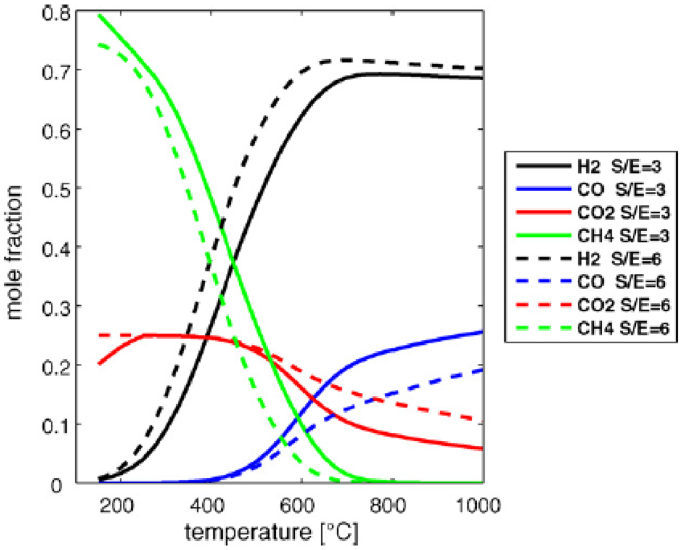
4. Modeling and simulation of ethanol autothermal reforming

In the last few years, there has been a great development in the computational area, increasing its participation in the solution of engineering problems, from faster, more accurate and graphical analyzes, reducing the costs and time spent on experiments (Martín, 2014; Dorf, Bishop, Canto S, Canto R, & Dormido, 2005; Graschinsky, Guinta, Amadeo, & Laborde, 2012).

The literature still has few modeling and simulation works with the proposal to better understand the process of autothermal reforming of ethanol, and most of the research on this study has focused on the development of new catalysts and new reactor configurations. (Baruah et al., 2015; Graschinsky et al., 2012; Rabenstein & Hacker, 2008).

Regarding the study of the thermodynamic model of the autothermal reforming of ethanol, Rabenstein and Hacker (2008) used the Peng-Robinson model for the process in the vapor / ethanol ratios of 3 and 6 with no oxygen and with the temperature variation, as shown in Figure 8.

Figure 8 – Simulation results for the composition of the autothermal reactor output with O_2 / C_2H_5OH = 0

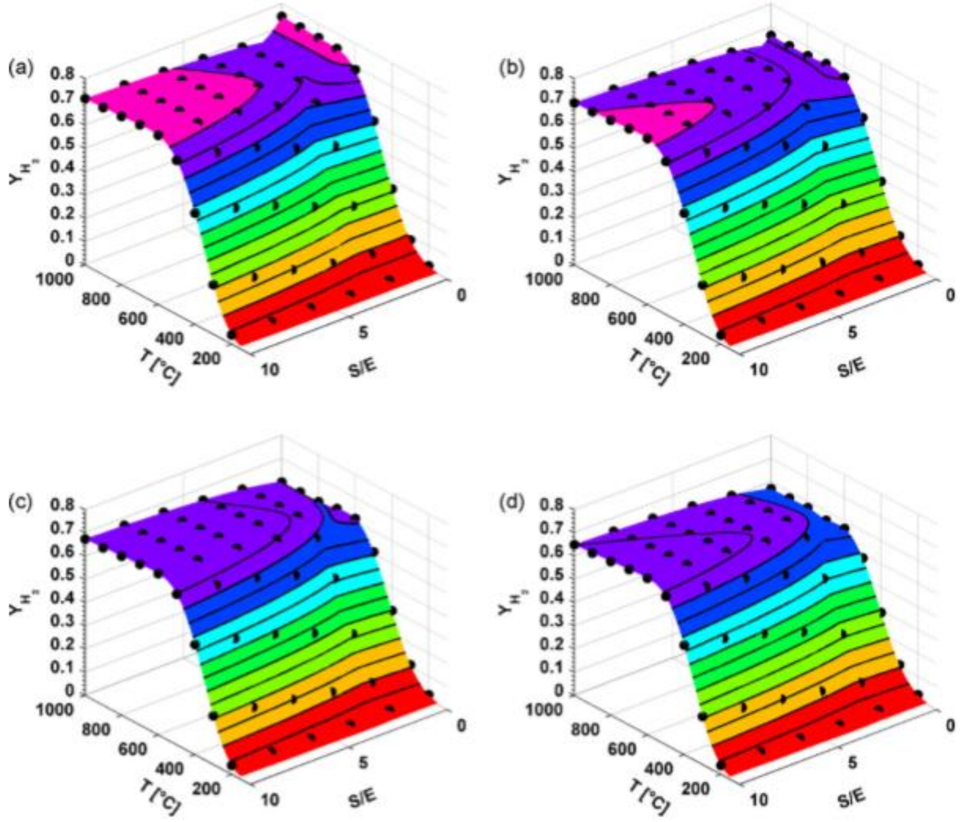


Source: Rabenstein and Hacker (2008)

Figures 8 shows that the production of hydrogen by authotermal reforming of etanol is enhaced with the increase in temperature and the steam/etanol ratio.

The results of the evaluation of the ethanol autothermal reforming in the presence of oxygen and variations in steam / ethanol ratios and temperature are represented in Figure 9.

Figure 9 – Simulations results for the molar fraction of H_2 at the autothermal reactor output as a function of temperature and vapor / ethanol ratio. a) Ro = 0; b) Ro = 0.25; c) Ro = 0.50; d) Ro = 0.75



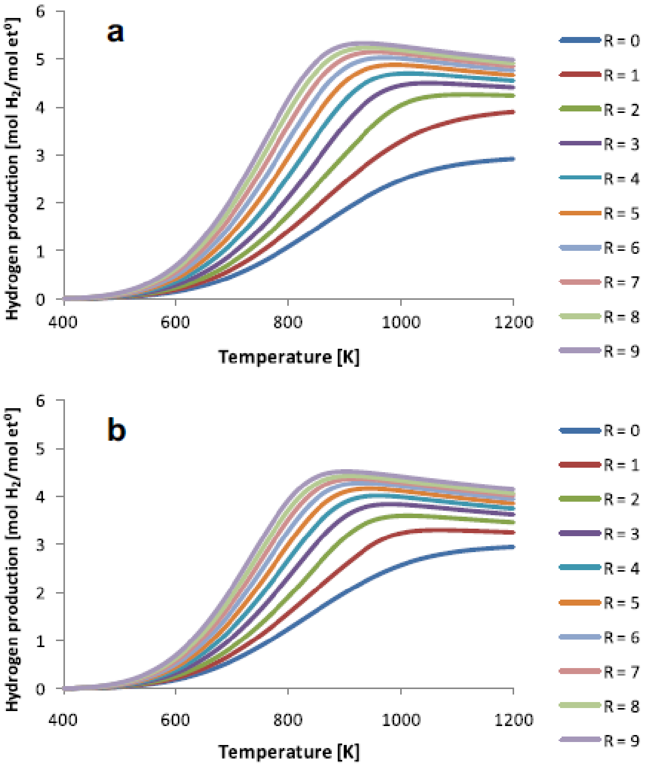
Source: Rabenstein and Hacker (2008)

Figure 9 shows again that the autothermal reforming of ethanol is favored by the increase in temperature and the steam/ethanol ratio. Meantime, the increase in oxygen/ethanol ratio reduces the production of hydrogen.

When analyzing Figures 8 and 9, it can be seen that the fraction of H_2 in the outlet flow of the reforming reactor is favored with the increase in temperature and steam / ethanol ratio, while it is impaired by the increase in flow and oxygen in the process. These conclusions were also found by Graschinsky et al. (2012) who presented a thermodynamic study of the ethanol autothermal reforming from the variation of its operational conditions.

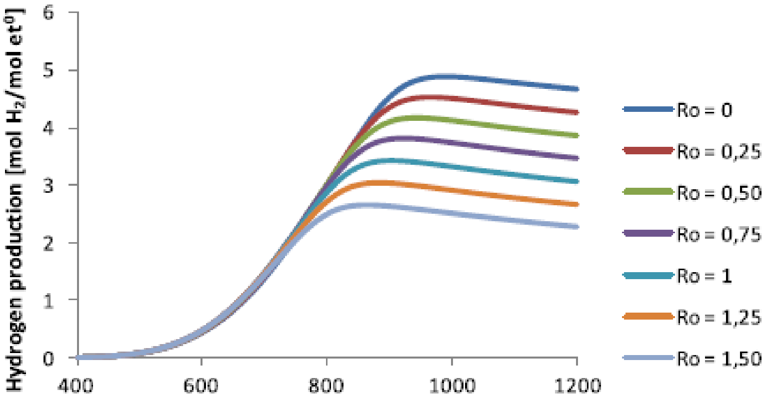
Figure 10 confirms, once more, that high temperatures and steam/etanol ratio enhace the hydrogen production. We can also observe that maximum hydrogen production in simulations dropped from more than 5 (mols H_2 / mols etanol) to less than 5 (mols H_2 / mols etanol) when the oxygen/etanol molar ratio increased from 0 to 0.5. Thus, the presence of oxygen decreases hydrogen production at this process.

Figure 10 – Simulations Results for the H_2 production at the autothermal reactor output as a function of temperature. R = 0-9. (a) Ro = 0; (b) Ro = 0.5



Source: Adapted from Graschinsky et al. (2012)

Figure 11 – Simulations results of H_2 production as a function of temperature. Ro = 0-1.5 and R = 5

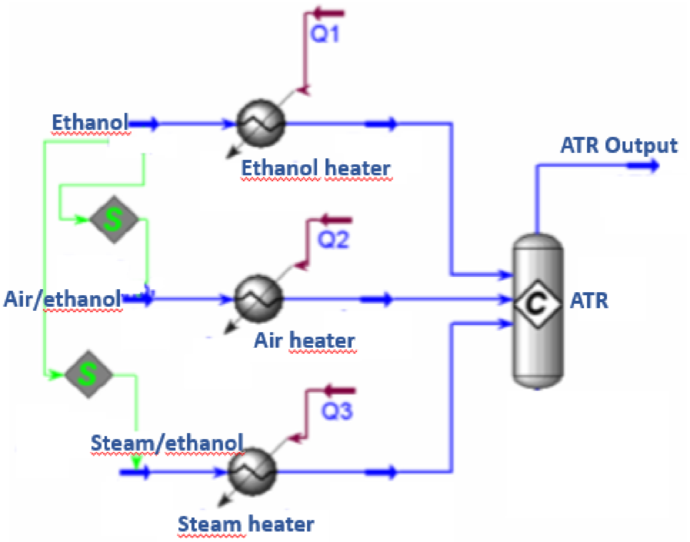


Source: Modified by Graschinsky et al. (2012)

Figure 11 shows that at fixed steam/ethanol molar ratio (5) the hydrogen production fell while the oxygen/ethanol ratio increased. We can also observe, once again, the positive influence of high temperatures on hydrogen production.

Almeida (2010) and Giwa (2013) performed the modeling of the ethanol autothermal reforming in process flow software.

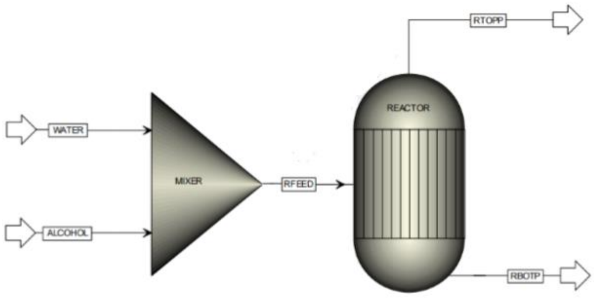
Figure 12 – Schematic representation of a process plant designed for simulation of an autothermal reactor in Aspen Hysys



Source: Modified by Almeida (2010)

Figures 12 shows the reagents being heated before entering the autothermal reactor and its output. Almeida (2010) also considered subsequent reactors in his modeling to increase the production of hydrogen and decrease the concentration of carbon monoxide formed in the process. The efficiency for the process simulated by him was 86.48%.

Figure 13 - Schematic representation of an alcohol reformer in Aspen Plus



Source: Modified from Giwa (2013)

Figure 13 illustrates an alcohol and water being mixed before entering the reforming reactor. Giwa (2013) evaluated the conversion of some alcohols in the process of autothermal reforming and found, for ethanol, a conversion close to 100% at temperatures above 430 °C. The studies carried out by Rabenstein and Hacker (2008), Almeida (2010), Graschinsky et al.,

(2012) and Giwa (2013) contribute to a better understanding of the autothermal reforming process of ethanol based on the study of hydrogen production according to operating conditions (temperature, steam / ethanol ratio, oxygen / ethanol ratio). However, these studies were made based on the univariable analysis of each operational condition, without combining the three variables at the same time. The analysis of the variables, separately, is not indicated when there is interaction, statistically significant, between them (Brito, Dias, Cunha, Ramos, & Teixeira, 2019) and in these studies, no statistical analysis was performed to verify whether or not there is an interaction between the studied variables or to determine the degree of influence that each one has on the production of hydrogen. Furthermore, these studies did not compare, technically and in close operational conditions, the hydrogen production of the ethanol autothermal reforming with the steam reforming of methane, a technology used on an industrial scale, in order to demonstrate how much the first process can be higher than the second. The presence of oxygen in the ethanol reforming, despite decreasing the production of hydrogen, can greatly reduce the consumption of external energy used in the reactor and the literature does not have studies that compare the production of hydrogen by the autothermal reforming of ethanol, carried out under conditions that they do not require external energy for the reactor, with the reforming of the methane, in order to verify if in this operational condition the autothermal reforming of the ethanol still produces greater amount of hydrogen than the reforming of the methane. Thus, the research carried out for catalysts, reactors, modeling and simulation of the ethanol autothermal reforming still have challenges and gaps to be filled in order to increase knowledge about the ethanol autothermal reforming, so that this process can become efficient and participate in the production of hydrogen at an industrial level.

5. Final considerations

The production of hydrogen from the ethanol autothermal reforming represents an alternative method to the steam reforming of methane that requires a large amount of external energy for the reactor and uses non-renewable raw material. Despite the potential presented by the autothermal reforming of ethanol, there are still many challenges to be solved so that this process can be carried out on an industrial scale in an efficient and economically viable manner.

This review article presented some of the main research carried out in recent years in order to overcome the main challenges of the autothermal reforming of ethanol. Among the most studied areas, it was clear that the most recent research is focused on the development of new catalysts, on the design of reactors and on the thermodynamics of the autothermal reforming of ethanol, based on computer modeling and simulation.

From the review presented here, it was noticed that in the last decade, there has been a considerable increase in studies regarding new catalysts based on non-noble metals. Some authors have managed to synthesize catalysts with non-noble (cheaper) metals and still achieve conversions of ethanol up to 100%, in addition to lower temperatures and good stability of these catalysts during the reforming reaction. In the case of the reactor design, the studies focus on the development of new structures that facilitate the permeability and meeting of the reagents so that higher conversion rates are obtained. In addition, the last decade has seen the development of reactors that can eliminate some purification stage, be it the purification of oxygen used in the process or even the separation between hydrogen and the by-products of the autothermal reforming of ethanol. Among these new reactors, there is a great interest in membrane reactors that have the ability to allow the removal of hydrogen during the reforming reaction, increasing the production of this gas and allowing the use of smaller scale industrial plants. In the field of modeling and simulation, research was concentrated on the thermodynamic study of the reaction of autothermal reforming of ethanol, investigating what are the best reasons among the reagents (ethanol, oxygen and steam) to obtain the highest hydrogen production, with simultaneous care with the energy expenditure of the reactor (which can be reduced by increasing the oxygen flow of the process).

In summary, the state-of-the-art review presented in this study showed the potential that the ethanol autothermal reforming has for the generation of hydrogen gas, based on the thermodynamic modeling and simulations of the process. In addition, it is possible to develop efficient and stable catalysts, synthesized from cheaper (non-noble) metals or combinations of noble and non-noble metals that can be used in the new reactor structures being developed. The combination of studies and advances obtained in these three best studied areas (reaction thermodynamics, catalysts and reactor design) contribute to making the process of ethanol autothermal reforming into an efficient and economically viable industrial technology, thus creating an alternative to the process of steam reforming of methane gas that has high energy expenditure and burning of a non-renewable raw material that emits carbon dioxide.

Although there are still obstacles in obtaining new efficient and inexpensive catalysts, in addition to reactors that maximize production. It is essential to increase research in simulation and modeling for the autothermal reforming of ethanol. This is because, with this type of study, it will be possible to better understand the thermodynamic conditions and if there are interactions between the operational conditions of the process. Once this knowledge is expanded, simple models can be obtained and whith them to adequately predict the production of hydrogen from variations in the operational conditions of the autothermal reformo f etanol.

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REFERENCES

Abokyi, E., Appiah-Konadu, P., Abokyi, F., & Oteng-Abayie, E. F. (2019). Industrial growth and emissions of CO_2 in Ghana: the role of financial development and fossil fuel consumption. *Energy Reports*, 5, 1339-1353.

Afolabi, A. T. F., Li, C.-Z., and Kechagiopoulos, P. N. (2019). Microkinetic modelling and reaction pathway analysis of the steam reforming of ethanol over ni/sio2. *International Journal of Hydrogen Energy*, 44(41):22816–22830.

Almeida, S. C. A. d. (2010). Simulação da reforma autotérmica do etanol para produção de hidrogênio. VI Congresso Nacional de Engenharia Mecânica.

Ballesteros, M. A., Daza, M. A., Valdés, J. P., Ratkovich, N., and Reyes, L. H. (2019). Applying pbl methodologies to the chemical engineering courses: Unit operations and modeling and simulation, using a joint course project. *Education for Chemical Engineers*.

Baruah, R., Dixit, M., Basarkar, P., Parikh, D., and Bhargav, A. (2015). Advances in ethanol autothermal reforming. *Renewable and Sustainable Energy Reviews*, 51:1345–1353.

Basile, A., Gallucci, F., Iulianelli, A., Tereschenko, G., Ermilova, M., and Orekhova, N. (2008). Ti–Ni–Pd dense membranes—the effect of the gas mixtures on the hydrogen permeation. *Journal of Membrane Science*, 310(1-2):44–50.

Brito, J. Q., Dias, F. d. S., Cunha, S. D., Ramos, L. P., and Teixeira, L. S. (2019). Multiple response optimization of alkaline pretreatment of sisal fiber (agave sisalana) assisted by ultrasound. *Biotechnology progress*, page e2802.

Cai, W., Wang, F., Zhan, E., Van Veen, A., Mirodatos, C., and Shen, W. (2008). Hydrogen production from ethanol over ir/ceo2 catalysts: a comparative study of steam reforming, partial oxidation and oxidative steam reforming. *Journal of Catalysis*, 257(1):96–107.

Chen, H., Yu, H., Peng, F., Yang, G., Wang, H., Yang, J., and Tang, Y. (2010). Autothermal reforming of ethanol for hydrogen production over perovskite $LaNiO_3$. *Chemical engineering journal*, 160(1):333–339.

Chen, H., Yu, H., Tang, Y., Pan, M., Yang, G., Peng, F., Wang, H., and Yang, J. (2009). Hydrogen production via autothermal reforming of ethanol over noble metal catalysts supported on oxides. *Journal of Natural Gas Chemistry*, 18(2):191–198.

Cormos, C.-C. (2014). Renewable hydrogen production concepts from bioethanol reforming with carbon capture. *International Journal of Hydrogen Energy*, 39(11):5597–5606.

da Silva, A. M., da Costa, L. O., Souza, K. R., Mattos, L. V., and Noronha, F. B. (2010). The effect of space time on Co/CeO_2 catalyst deactivation during oxidative steam reforming of ethanol. *Catalysis Communications*, 11(8):736–740.

de Lima, S. M., da Silva, A. M., da Costa, L. O., Assaf, J. M., Mattos, L. V., Sarkari, R., Venugopal, A., and Noronha, F. B. (2012). Hydrogen production through oxidative steam reforming of ethanol over Ni-based catalysts derived from La1- $xCexNiO_3$ perovskite-type oxides. *Applied Catalysis B: Environmental*, 121:1–9.

Divins, N. J., López, E., Rodríguez, A., Vega, D., and Llorca, J. (2013). Bio-ethanol steam reforming and autothermal reforming in 3-µm channels coated with $rhpd/CeO_2$ for hydrogen generation. *Chemical Engineering and Processing: Process Intensification*, 64:31–37.

Dorf, R. C., Bishop, R. H., Canto, S. D., Canto, R. D., and Dormido, S. (2005). *Sistemas de control moderno*. Pearson Prentice Hall.

Đozić, D. J., & Urošević, B. D. G. (2019). Application of artificial neural networks for testing long-term energy policy targets. *Energy*, 174, 488-496.

Elbadawi, A. H., Ge, L., Zhang, J., Zhuang, L., Liu, S., Tan, X., Wang, S., and Zhu, Z. (2019). Partial oxidation of methane to syngas in catalytic membrane reactor: Role of catalyst oxygen vacancies. *Chemical Engineering Journal*, page 123739.

FAHIM, M. A., AL-SAHHAF, T. A., and ELKILANI, A. S. (2012). Introduçãoo ao refino de petróleo. Rio de Janeiro: *Editora Campus.*

Fischer, C. D. and Iribarren, O. A. (2017). Oxygen integration of autothermal reforming of ethanol with oxygen production, through ion transport membranes in counter current configuration. *Computers & Chemical Engineering*, 99:245–254.

Fischer, G., Shah, M., N. Tubiello, F., & Van Velhuizen, H. (2005). Socio-economic and climate change impacts on agriculture: an integrated assessment, 1990–2080. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 360(1463), 2067-2083.

Furtado, A. C., Alonso, C. G., Cantao, M. P., and Fernandes-Machado, N. R. C. (2011). Support influence on Ni–Cu catalysts behavior under ethanol oxidative reforming reaction. *International Journal of Hydrogen Energy*, 36(16):9653–9662.

Gallucci, F., Annaland, M. V. S., and Kuipers, J. (2010). Pure hydrogen production via autothermal reforming of ethanol in a fluidized bed membrane reactor: a simulation study. *International Journal of Hydrogen Energy*, 35(4):1659–1668.

Giwa, A. G. O. (2013). Application of aspen plus to hydrogen production from alcohols by steam reforming: Effects of reactor temperature. *International Journal of Engineering*, 2(8).

Graschinsky, C., Giunta, P., Amadeo, N., and Laborde, M. (2012). Thermodynamicanalysis of hydrogen production by autothermal reforming of ethanol. *International Journal of Hydrogen Energy*, 37(13):10118–10124.

Greluk, M., Rybak, P., S lowik, G., Rotko, M., and Machocki, A. (2015). Comparativestudy on steam and oxidative steam reforming of ethanol over 2KCO/ZrO_2 catalyst. *Catalysis Today*, 242:50–59.

Hartmann, M., Maier, L., Minh, H., and Deutschmann, O. (2010). Catalytic partial oxidation of iso-octane over rhodium catalysts: An experimental, modeling, and simulation study. *Combustion and Flame*, 157(9):1771–1782.

Herbert, G. J. and Krishnan, A. U. (2016). Quantifying environmental performance of biomass energy. *Renewable and Sustainable Energy Reviews*, 59:292–308.

Holladay, J. D., Hu, J., King, D. L., and Wang, Y. (2009). An overview of hydrogen production technologies. *Catalysis today*, 139(4):244–260.

Huang, L., Xie, J., Chen, R., Chu, D., and Hsu, A. T. (2010). Nanorod alumina-supported Ni–Zr–Fe/Al_2O_3 catalysts for hydrogen production in auto-thermal reforming of ethanol. *Materials Research Bulletin*, 45(1):92–96.

Hung, C.-C., Chen, S.-L., Liao, Y.-K., Chen, C.-H., and Wang, J.-H. (2012). Oxidative steam reforming of ethanol for hydrogen production on M/Al_2O_3. *International Journal of Hydrogen Energy*, 37(6):4955–4966.

Iulianelli, A. and Basile, A. (2019). Advances on inorganic membrane reactors for production of hydrogen. *Fuel Cells and Hydrogen Production: A Volume in the Encyclopedia of Sustainability Science and Technology, Second Edition*, pages 935–945.

Iulianelli, A., Dalena, F., & Basile, A. (2019). Steam Reforming, Preferential Oxidation, and Autothermal Reforming of Ethanol for Hydrogen Production in Membrane Reactors. *In Ethanol* (pp. 193-213). Elsevier.

Iulianelli, A., Ribeirinha, P., Mendes, A., and Basile, A. (2014). Methanol steam reforming for hydrogen generation via conventional and membrane reactors: a review. *Renewable and Sustainable Energy Reviews*, 29:355–368.

Jin, Y., Rui, Z., Tian, Y., Lin, Y. S., & Li, Y. (2016). Autothermal reforming of ethanol in dense oxygen permeation membrane reactor. *Catalysis Today*, 264, 214-220.

Jin, Y., Rui, Z., Tian, Y., Lin, Y., and Li, Y. (2010). Sequential simulation of dense oxygen permeation membrane reactor for hydrogen production from oxidative steam reforming of ethanol with aspen plus. *International journal of hydrogen energy*, 35(13):6691–6698.

Lin, W.-H., Liu, Y.-C., and Chang, H.-F. (2010). Autothermal reforming of ethanol in a Pd–Ag/Ni composite membrane reactor. *International Journal of Hydrogen Energy*, 35(23):12961–12969.

Liu, Y., Lin, R., Man, Y., and Ren, J. (2019). Recent developments of hydrogen production from sewage sludge by biological and thermochemical process. *International Journal of Hydrogen Energy. Accepted manuscript.*

Martín, M. M. (2014). *Introduction to software for chemical engineers*. CRC Press.

Martinelli, M., Watson, C. D., and Jacobs, G. (2019). Sodium doping of Pt/M-ZrO_2 promotes c–c scission and decarboxylation during ethanol steam reforming. *International Journal of Hydrogen Energy*.

Muritala, I. K., Guban, D., Roeb, M., and Sattler, C. (2019). High temperature production of hydrogen: Assessment of non-renewable resources technologies and emerging trends. *International Journal of Hydrogen Energy*.

Nahar, G. and Dupont, V. (2014). Hydrogen production from simple alkanes and oxygenated hydrocarbons over ceria–zirconia supported catalysts. *Renewable and Sustainable Energy Reviews*, 32:777–796.

Nourbakhsh, H., Shahrouzi, J. R., Ebrahimi, H., Zamaniyan, A., and Nasr, M. R. J. (2019). Experimental and numerical study of syngas production during premixed and ultra-rich partial oxidation of methane in a porous reactor. *International Journal of Hydrogen Energy*, 44(60):31757–31771.

Parry, M. L., Rosenzweig, C., Iglesias, A., Livermore, M., & Fischer, G. (2004). Effects of climate change on global food production under SRES emissions and socio-economic scenarios. *Global environmental change*, 14(1), 53-67. *processing*. Elsevier.

Rabenstein, G. and Hacker, V. (2008). Hydrogen for fuel cells from ethanol by steam-reforming, partial-oxidation and combined auto-thermal reforming: A thermodynamic analysis. *Journal of Power Sources*, 185(2):1293–1304.

Sáez-Martínez, F. J., Lefebvre, G., Hernández, J. J., and Clark, J. H. (2016). Drivers of sustainable cleaner production and sustainable energy options. *Journal of cleaner production*, 138:1–7.

Santucci, A., Annesini, M. C., Borgognoni, F., Marrelli, L., Rega, M., and Tosti, S. (2011). Oxidative steam reforming of ethanol over a Pt/Al_2O_3 catalyst in a Pd-based membrane reactor. *International Journal of Hydrogen Energy*, 36(2):1503–1511.

Shekhawat, D., Spivey, J. J., and Berry, D. A. (2011). *Fuel cells: technologies for fuel*

Sinigaglia, T., Freitag, T. E., Kreimeier, F., and Martins, M. E. S. (2019). Use of patentsas a tool to map the technological development involving the hydrogen economy. *World Patent Information,* 56:1–8.

Smith, P., Bustamante, M., Ahammad, H., Clark, H., Dong, H., Elsiddig, E. A., ... & Masera, O. (2014). Agriculture, forestry and other land use (AFOLU). *In Climate change 2014: mitigation of climate change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.* Cambridge University Press.

Song, C. (2002). Fuel processing for low-temperature and high-temperature fuel cells: Challenges, and opportunities for sustainable development in the 21st century. *Catalysis today*, *77*(1-2), 17-49.

Tosti, S., Zerbo, M., Basile, A., Calabr`o, V., Borgognoni, F., and Santucci, A. (2013). Pd-based membrane reactors for producing ultra-pure hydrogen: oxidative reforming of bio-ethanol. *International Journal of Hydrogen Energy*, 38(1):701–707.

Vita, A., Pino, L., Italiano, C., and Palella, A. (2019). Steam reforming, partial oxidation, and autothermal reforming of ethanol for hydrogen production in conventional reactors. *In Ethanol*, pages 159–191. Elsevier.

VLĂDAN, S. I., Isopencu, G., Jinescu, C., & MAREŞ, M. A. (2011). Process simulation to obtain a synthesis gas with high concentration of hydrogen. *Gas*, 5, 7.

Wang, C.-H., Ho, K.-F., Chiou, J. Y., Lee, C.-L., Yang, S.-Y., Yeh, C.-T., and Wang, C.-B. (2011). Oxidative steam reforming of ethanol over PtRu/ZrO_2 catalysts modified with sodium and magnesium. *Catalysis Communications*, 12(10):854–858.

Xuan, J., Leung, M. K., Leung, D. Y., and Ni, M. (2009). A review of biomass-derived fuel processors for fuel cell systems. *Renewable and Sustainable Energy Reviews*, 13(6-7):1301–1313.

Xue, Z., Shen, Y., Li, P., Pan, Y., Li, J., Feng, Z., Zhang, Y., Zeng, Y., Liu, Y., and Zhu, S. (2018). Promoting effects of lanthanum oxide on the NiO/CeO_2 catalyst for hydrogen production by autothermal reforming of ethanol. *Catalysis Communications,* 108:12–16.

Yamazaki, Y., Maruko, S., and Komori, S. (2011). Oxidative autothermal reformer and oxidative autothermal reforming method using the same. US Patent 7,981,372.

Yun, S., Lim, H., and Oyama, S. T. (2012). Experimental and kinetic studies of the ethanol steam reforming reaction equipped with ultrathin pd and Pd–Cu membranes for improved conversion and hydrogen yield. *Journal of membrane science*, 409:222–231.

Zhou, Y., Chen, X., Tan, X., Liu, C., Zhang, S., Yang, F., ... & Huang, H. (2018). Mechanism of CO_2 Emission Reduction by Global Energy Interconnection. *Global Energy Interconnection*, 1(4), 409-419.

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