Optimization of hydrogen production with CO₂ capture by autothermal chemical-looping reforming using different bioethanol purities

E. García-Díez^a, F. García-Labiano^{*a}, L. F. de Diego^a, A. Abad^a, P. Gayán^a, J. Adánez^a, J.A.C. Ruíz^b

^a Department of Energy and Environment, Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, E-50018 Zaragoza, Spain.

^b Centro de Tecnologias do Gás e Energias Renováveis (CTGAS-ER), Av. Capitão Mor Gouveia, Natal, Brazil

* Corresponding authors: Tel.: +34 976 733 977; fax: +34 976 733 318,

E-mail address: glabiano@icb.csic.es (F. García-Labiano).

Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, E-50018 Zaragoza, Spain.

Abstract:

Autothermal Chemical-Looping Reforming (a-CLR) is a process which allows hydrogen production avoiding the environmental penalty of CO₂ emission typically produced in other processes. The major advantage of this technology is that the heat needed for syngas production is generated by the process itself. This heat necessary for the endothermic reactions is supplied by a Ni-based oxygen-carrier (OC) circulating between two reactors: the air reactor (AR), where the OC is oxidized by air, and the fuel

reactor (FR), where the fuel is converted to syngas. Other important advantage is that this process also allows the production of pure N_2 in the AR outlet stream. A renewable fuel such as bioethanol was chosen in this work due to their increasing worldwide production and the current excess of this fuel presented by different countries.

In this work, mass and heat balances were done to determine the auto-thermal conditions that maximize H_2 production, assuming that the product gas was in thermodynamic equilibrium. Three different types of bioethanol has been considered according to their ethanol purity; Dehydrated ethanol (≈ 100 vol.%), hydrated ethanol (≈ 96 vol.%), and diluted ethanol (≈ 52 vol.%). It has been observed that the higher H_2 production (4.62 mol of H_2 per mol of EtOH) has been obtained with the use of diluted ethanol and the surplus energy needed could be compensated by the energy save achieved during the purification of ethanol in the production process.

Keywords: Hydrogen production; CO_2 capture; Chemical-looping reforming; Oxygen-carrier; Bioethanol; Heat balance.

1. Introduction:

The greenhouse gas problematic has become more relevant for the last several decades. The concentration of carbon dioxide in the atmosphere has recently reached values over 400 ppm and it is continuously increasing [1, 2], becoming extremely urgent new alternatives to ensure the reduction of greenhouse gas emissions.

One of the main causes of the increase of the CO_2 concentration is the diffuse emissions associated to the transport sector with the 21% of the global CO_2

emissions [3]. The use of hydrogen is one alternative that is currently studied to reduce the CO₂ emissions from mobile sources [4]. Hydrogen is an energy vector which implies that it has to be obtained from a primary energy sources, being the most common method the steam methane reforming (SMR) with almost the half worldwide production [5]. In this process the reforming reaction takes place inside tubes packed with Ni catalyst [6]. However, additional methane is burnt into a combustor to produce the heat required for the process and, as a consequence, large amounts of CO₂ are emitted into the atmosphere. In fact, Soltani et al. [7] reported that almost 7 kg of CO₂ per kg of H₂ are produced in a SMR process, becoming responsible for 3% of the total CO₂ emissions from industrial sector. A possible solution is the use of the carbon capture and storage (CCS) technologies, especially the use of amines although these processes are usually associated to high economic penalties.

An alternative to avoid CCS technologies is the auto-thermal reforming (ATR) process [5] in which methane, water and pure oxygen are injected into an adiabatic reactor where the reforming reaction and the partial oxidation of the methane take place. This last exothermic reaction produces the heat needed for the endothermic reforming reaction. However, the air separation unit (ASU) needed to produce the oxygen implies a high energy consumption and costs. For instance, for an oxy-coal system with a fuel heat input of 1502 MW, the ASU capacity requirement is 87 MW, which represents an ASU investment cost of 258 M\$, an ASU energy consumption of 685 kJ/kg O₂ or a 8% points penalty for net electrical efficiency [8]. A possibility to supply oxygen for hydrogen/syngas production with low environmental or energy penalties is the use chemical looping process [9]. The

autothermal Chemical-Looping Reforming (a-CLR) was initially proposed by Mattison and Lyngfelt [10] as a hydrogen production process with no CO₂ emissions to the atmosphere and no external heat required for the process. It is based on the use of an oxygen carrier (OC), usually a metal oxide, which transfers the oxygen from the air to the fuel avoiding the direct contact between them. The oxygen carrier used circulates between two interconnected fluidized bed reactors: Fuel reactor (FR) and Air reactor (AR). In the FR the fuel is transformed to the reformer gas (H₂, CO, CO₂, CH₄ and H₂O). The reduced oxygen carrier is transferred to the AR where it is regenerated with air being ready for a new cycle. Furthermore, to maximize the syngas production with no extra heat needed nor extra heat produced it is imperative to determine the autothermal conditions of the process. The heat required for all endothermic reactions taken place in the FR is provided by the hot solids coming from the AR, which have been heated by the exothermic regeneration reaction.

The use of the proper oxygen carrier is one of the keys of any Chemical looping process. For the CLR process the OC used must have not only oxygen transfer capacity but also reforming catalytic activity. Although several materials based on Cu and Fe are currently tested to produce hydrogen [11, 12], Ni-based oxygen carriers have shown the best results for chemical looping reforming [13, 14] due to their high selectivity to syngas production.

The major experience in a-CLR process has been reached using gaseous fuels [15]. However, liquid fuels are becoming more relevant in the hydrogen production process in CLR processes. García-Labiano et al. [16] evaluated the use of ethanol

and Dou, Chen et al. [17] the use of glycerol as fuel in CLR processes. Moldenhauer et al. [18] tested the CLR using kerosene to produce H_2 .

Among the possible liquid fuels, those that are produced using renewable energies, such as bioethanol or biodiesel, offer great expectations (bio-CCS) due to the possibility of producing negative CO_2 emissions by the combination of CCS technologies and biomass as fuel [19]. Bioethanol presents high possibilities based on the large amount available, being United States and Brazil the major worldwide producers, and it is expected that production will increase in the future [20].

In any reforming process, H_2O is fed to maximize hydrogen production. In this particular process, the water could be fed in the FR or in a WGS reactor located downstream the FR. The place and amount of water fed presents an important influence on the mass and heat balance and in the H_2 production. H_2O is usually fed into the WGS reactor. However, new options are available in those cases where the fuel, obtained from renewable sources, has already water.

It must be considered that the product obtained from the biomass fermentation has a concentration of 10 vol.% of bioethanol. After that, this is distilled until the azeotrope point producing what is called hydrated bioethanol, with a concentration of 95.57 vol.% [21]. This hydrated bioethanol suffers a zeotropic distillation to produce the dehydrated bioethanol, with a concentration of 99.5 vol.% [21]. Obviously, these concentration processes require from a large amount of energy. The energy required to eliminate the water from the bioethanol produced by fermentation is the $\approx 37\%$ of the used in the global bioethanol production process [22-25]: the distillation requires the $\approx 23\%$ and the azeotrope distillation the $\approx 14\%$

because the energy necessary for water removal increases exponentially when the purity of the bioethanol is near to the azeotrope point.

Hence, the use of hydrous bioethanol in a CLR system presents a novel strategy to produce hydrogen with inherent CO₂ capture which also implies an interesting energy advantage in the bioethanol production process. Up to now, all the works existing in the literature for hydrogen production using liquid fuels by the CLR process were focused on the evaluation of the fuel, and did not determine neither the autothermal conditions nor the maximum hydrogen production.

The objective of this work was therefore to determine the auto-thermal operational conditions that maximize H₂ production in a global process including the autothermal chemical looping reforming and a water gas shift reactor (a-CLR + WGS), using bioethanol as fuel. In addition, different water-to-ethanol relationships were evaluated in order to determine the viability of the use of hydrated and diluted ethanol to take advantage of the water contained in the fuel which could imply important energy saving during the fuel production process. Mass and heat balances were done to analyze the effect of the main operating conditions, such as the oxygen-to-ethanol and water-to-ethanol molar ratios, the solid circulation rate, and the nickel oxide content of the oxygen carrier.

2. Methods

Fig. 1 shows a general diagram of the system considered in this work. It integrates the bioethanol production process and a global H₂ production process, composed by an a-CLR system, a WGS reactor, and several heat exchangers. The mass and heat

balances will be made only in the global H_2 production process. In this case, the sensible heat of the outlet streams is used in the heat exchangers to evaporate and preheat the inlet reactants. Depending on the operational conditions, H_2 and surplus heat could be recovered from the global system which could be used in the bioethanol production process.

The following assumptions were done in the base case:

- The system is at steady state.
- No heat losses were considered.
- The temperature in the FR (T_{FR}) was 900 °C.
- The temperature in the WGS reactor was 250 °C.
- The temperature at the FR and AR inlet streams were 477 °C.
- All the outlet streams were cooled to 100 °C.
- The molar flow of pure ethanol in the FR was 1 mol/s.
- The nickel oxide content of the OC was 20 wt.% supported on alumina.
- The solid circulation rate, F_S , was fixed at 2.75 kg/s or 2.38 kg/s·MW.
- The oxygen-to-ethanol ($O_{NiO}/EtOH$) molar ratio was controlled by limiting the oxygen introduced to the AR. As a consequence, all oxygen fed to the a-CLR system reacts with the reduced oxygen carrier and pure N_2 was obtained at the AR outlet stream.
- The water-to-ethanol ($H_2O/EtOH$) molar ratio fed into the WGS reactor was 3.

2.1 Reactions considered in the CLR process

In any chemical looping process the main parameter to be considered is the molar relationship between the oxygen reacted in the FR and the fuel injected, defined in

this case as the oxygen-to-ethanol molar ratio ($O_{NiO}/EtOH$). Based on the value of this ratio, different reactions would take place in the FR, producing different syngas composition. Fig 2. shows the products obtained in thermodynamic equilibrium as a function of the $O_{NiO}/EtOH$ molar ratio with two different $H_2O/EtOH$ molar ratios (0 and 3). The HSC Chemistry 6.1 software [26] has been used for the calculations.

For $O_{NiO}/EtOH > 6$, the main reaction that takes place in the FR is the complete combustion of the ethanol (R.1), and other possible gaseous intermediates (R.2-R.4) giving as final products CO_2 and H_2O .

If the $1 < O_{NiO}/EtOH < 6$ the contribution of the complete combustion reaction (R.1) becomes lower and the partial oxidation of ethanol (R.5) shows up producing more syngas.

At the same time, the reforming reactions (R.6-R.9) catalyzed by metallic Nickel produced in reactions (R.1-R.5), take place increasing the hydrogen production.

If $O_{NiO}/EtOH < 1$ there would not be enough oxygen in the FR to oxidize the ethanol and it would be produced the decomposition reaction of the fuel. According to

Fatsikostas et al. [27] ethanol suffers carbon break change reactions to produce lighter hydrocarbons as intermediates during decomposition in presence of alumina and nickel, giving finally syngas and carbon (R.10-R.12).

This carbon obtained could be gasified in presence of water or CO_2 inside the fuel reactor:

Furthermore, the water gas shift (WGS) reaction must be considered.

In the AR the regeneration of the metallic Ni by the oxidation reaction (R.16) takes place. In addition, when carbon is formed in the fuel reactor, it is transferred with the oxygen carrier to the AR where it would react with oxygen producing CO_2 (R.17), decreasing the carbon capture efficiency of the chemical looping process.

This carbon formation is obtained with an $\text{O}_{\text{NiO}}/\text{EtOH} \leq 1$ when the $\text{H}_2\text{O}/\text{EtOH}$ molar ratio is 0. However, if this relationship is equal to 3, no carbon formation is observed (see Fig 2). Hence, different $\text{H}_2\text{O}/\text{EtOH}$ molar ratios imply different operating ranges of $\text{O}_{\text{NiO}}/\text{EtOH}$ for a chemical looping reforming. In any case, these values have to be between the lowest one that avoids the carbon formation and 6.

2.2 Mass and heat balance in the a-CLR system

Based on the oxygen mass balance the oxygen given by the air injected is equal to the oxygen captured by the OC in the AR and equal to the oxygen that reacts in the fuel reactor with the ethanol:

$$\text{Oxygen}_{\text{air,AR}} = \text{Oxygen}_{\text{OC,AR}} = \text{Oxygen}_{\text{OC,FR}} \quad (1)$$

$$F_{\text{O}_2,\text{in}} \Delta X_{\text{O}_2} = \frac{F_s x_{\text{NiO,ox}}}{M_{\text{NiO}}} \Delta X_s \quad (2)$$

$$\frac{F_s x_{\text{NiO,ox}}}{M_{\text{NiO}}} \Delta X_s = F_{\text{EtOH}} \frac{O_{\text{NiO}}}{\text{EtOH}} \quad (3)$$

where $F_{\text{O}_2,\text{in}}$ is the molar flow of oxygen at the inlet of the AR, M_{NiO} is the molecular weight of NiO, F_s is the oxygen carrier circulation flow-rate, $x_{\text{NiO,ox}}$ is the NiO content when the OC is complete oxidized, F_{EtOH} is the molar flow of EtOH fed to the FR and the $O_{\text{NiO}}/\text{EtOH}$ molar ratio is the amount of oxygen transferred by the oxygen carrier to the fuel reactor per mol of ethanol fed.

The oxygen fed conversion, ΔX_{O_2} , was defined as:

$$\Delta X_{\text{O}_2} = \frac{F_{\text{O}_2,\text{in}} - F_{\text{O}_2,\text{out}} - F_{\text{CO}_2,\text{out}}}{F_{\text{O}_2,\text{in}}} \quad (4)$$

where $F_{\text{O}_2,\text{out}}$ is the molar flow of oxygen at the outlet of the AR. $F_{\text{CO}_2,\text{out}}$ corresponds to the molar flow of CO_2 produced by the combustion of the possible carbon formed in the FR through reaction (R.17).

Otherwise, the oxygen carrier conversion variation, ΔX_s , was written as:

$$\Delta X_s = X_{\text{AR}} - X_{\text{FR}} \quad (4)$$

where X_{AR} and X_{FR} are the conversion of the oxygen carrier at the outlet of the air and fuel reactor respectively, which could be calculated as:

$$X_{AR} = \frac{x_{NiO,AR} - x_{NiO,red}}{x_{NiO,ox} - x_{NiO,red}} \quad (5)$$

$$X_{FR} = \frac{x_{NiO,FR} - x_{NiO,red}}{x_{NiO,ox} - x_{NiO,red}} \quad (6)$$

where $x_{NiO,AR}$ and $x_{NiO,FR}$ are the NiO content of the oxygen carrier at the outlet of the air and fuel reactor respectively. $x_{NiO,ox}$ and $x_{NiO,red}$ are the NiO contents when the oxygen carrier is complete oxidized and reduced.

The composition of the syngas produced was calculated that the product gas was in the thermodynamic equilibrium, which was calculated using the method of minimization of the Gibbs free energy with the HSC Chemistry 6.1 software [26]. In a previous work [16] it was determined that the syngas composition obtained was very close to the defined by the thermodynamic equilibrium.

Moreover, the heat balance was expressed as:

$$\Delta H_{CLR} = \Delta H_{FR} + \Delta H_{AR} \quad (7)$$

where ΔH_{FR} and ΔH_{AR} are the variation of enthalpy associated to all gases and solids inside the fuel reactor and air reactor respectively, and the ΔH_{CLR} is the energy required to remove or give to the CLR system.

$$\Delta H_j = \sum n_i h_i \quad (8)$$

where n_i is the number of moles and the enthalpy of each component, h_i , was obtained according to:

$$h_i = h_{oi} + \int_{298}^T C_{p_i}(T) dT \quad (9)$$

with h_{oi} as the standard enthalpy, T the operating temperature and the C_{p_i} the specific heat of each component. All thermochemical data were obtained from Barin [28]. All gases (EtOH, CH₄, CO, CO₂, H₂, H₂O, N₂, O₂) and solids (NiO, Ni,

Al₂O₃) present in the reactors were considered as reactants and products for the heat balance.

According to the equation (7) the process is autothermic when ΔH_{CLR} is equal to 0, i.e. $\Delta H_{\text{a-CLR}}$. If $\Delta H_{\text{CLR}} > 0$ it means the heat in the AR is not enough to fulfill the heat balance i.e., extra heat is needed for the reactions (R.1-R.9) in the process. Otherwise, when $\Delta H_{\text{CLR}} < 0$ it means that there is excess of heat in the system in the CLR system.

2.3. Mass and heat balance in the global system

Once the mass and heat balances in the a-CLR system were determined, they had to be integrated in the global process including the WGS reactor and the preheaters.

The global heat balance, ΔH_{G} , was defined as

$$\Delta H_{\text{G}} = \Delta H_{\text{a-CLR}} + \sum \Delta H_{\text{HE}} + \Delta H_{\text{WGS}} \quad (10)$$

where ΔH_{HE} and ΔH_{WGS} are the variation of enthalpy associated to each heat exchanger used in the process and in the WGS reactor. It must be remembered that the value of $\Delta H_{\text{a-CLR}}$ in the auto-thermal process is zero.

3. Results and discussion

First it will be shown the results of H₂ production from pure bioethanol and feeding the H₂O into the WGS reactor. Later, it will be analyzed the possibility of using hydrated bioethanol due to the advantages related to energy costs.

3.1 Mass and heat balances in a-CLR with pure bioethanol

The mass and heat balances were done to obtain the autothermal conditions in the CLR system (a-CLR) using pure ethanol as fuel and without water addition

($H_2O/EtOH=0$). An OC with a NiO content of 20 wt.% was considered. The solid circulation rate was fixed to 2.38 kg/s·MW (2.75 kg/s). Firstly, it was studied the effect of the $O_{NiO}/EtOH$ molar ratio on the AR temperature, T_{AR} , (T_{FR} was fixed at 900 °C), on the heat balance, and on the hydrogen production after the water gas shift reactor (using a $H_2O/EtOH=3$ in the WGS reactor). The results obtained are showed in Fig 3.

A decrease in the $O_{NiO}/EtOH$ molar ratio produces an increase in the ΔH of the CLR system, an increase of the T_{AR} , and an increase of the H_2 production after the WGS reactor. A $H_2O/EtOH$ molar ratio equal to 3 was used due to the stoichiometric of the reaction (R.7).

In this case, the autothermal conditions in the CLR were achieved at an $O_{NiO}/EtOH$ molar ratio of 1.47. At these conditions, the T_{AR} was 992 °C, and a H_2 production of 4.46 mol per mol of bioethanol. Lower values would produce higher H_2 production but external heat would be required in the CLR system.

3.2. Effect of the solid circulation rate, F_s

According to the eq. (2 and 3) it can be transferred the same oxygen if the factor $F_s \cdot x_{NiO} \cdot \Delta X$ is constant. It was previously obtained the a-CLR for a particular F_s , which means a specific value of ΔX_s , and an OC with a NiO content of 20 wt.%. However, the a-CLR could be obtained for different F_s and OC. Hence, it has been analyzed how both variables affect the H_2 production.

Fig 4 shows the relation existing among the solids circulation rates (F_s), and the solid conversion variation (ΔX_s), the AR temperature, the $O_{NiO}/EtOH$ molar ratio and the H_2 production, for oxygen carriers with four different NiO contents (5-10-20-40 wt.%).

According to equation 3, an increase in the solid circulation rate (F_s) implies a decrease in the solid variation conversion (ΔX_s) for a given OC ($x_{NiO}=\text{constant}$), and a decrease in the T_{AR} and an increase in the H_2 production. The use of OC with different NiO content produces changes on the ΔX to maintain the same oxygen balance (eq. 3), and slight variations in the T_{AR} and H_2 production. The slight differences observed in the T_{AR} (Fig 4.b.) are caused by the different specific heat derived from the different solid composition. Based on these results, F_s was demonstrated to be the most affecting variable on heat balance, being the NiO content of minor relevance.

As observed in Fig 4 there is a width range of F_s that fulfill the a-CLR conditions. The operational restrictions are associated to very high T_{AR} or solid circulation rates. In this work, temperatures above 1050 °C or solid circulation rates higher than 17 kg/s·MW [29] have been considered as the limit for the common operating conditions in this type of installations. In the operational range from 1.7-17 kg/s·MW, a production of H_2 about 4.44 - 4.49 was obtained at a-CLR conditions with any Ni-based material.

3.3 Effect of the bio-ethanol purity

The above study was done considering the feeding of the water in the WGS reactor. However, there is also the possibility of feeding part or all water required for the complete reforming reaction (R.7) into the FR. In this case, it would not be necessary the total elimination of water from the product obtained by the fermentation process, implying an important energy save in the fuel production process. From the dehydrated bioethanol with a purity close to the 100 vol.%, it could be used the hydrated bioethanol with a maximum concentration of 95.6 vol.%

[25], or a diluted bioethanol with 51.8 vol.%, which allows feeding all water directly to the FR.

Mass and heat balances were done to the global a-CLR system varying the amount of water in the inlet of both FR and WGS keeping the total $\text{H}_2\text{O}/\text{EtOH}$ ratio in the global system equal to 3. Fig 5 shows the H_2 production in the global process and the T_{AR} as a function of the $\text{H}_2\text{O}/\text{EtOH}$ molar ratio fed in the FR and WGS.

No difference in the AR temperature was observed considering that the F_s was maintained constant. However, the amount of H_2 produced decreases if more water is fed to FR instead of the WGS reactor.

The addition of water in the FR implies that more energy is needed to heat it up to reach the T_{FR} . This extra energy was achieved increasing the $\text{O}_{\text{NiO}}/\text{EtOH}$ molar ratio, which means a higher contribution of the complete combustion (R.1) in the process.

It has been also identified the three different types of purities above mentioned. The dehydrated with a $\text{H}_2\text{O}/\text{EtOH}=0$, hydrated with a $\text{H}_2\text{O}/\text{EtOH}=0.2$, and diluted bioethanol with a $\text{H}_2\text{O}/\text{EtOH}=3$.

3.4 Effect of FR temperature

The T_{FR} is an important operating condition affecting reaction rates and equilibrium constant (k_{eq}), ie. equilibrium in the gas phase.

Fig 6 shows the $\text{O}_{\text{NiO}}/\text{EtOH}$ molar ratio to achieve the a-CLR system and the minimum $\text{O}_{\text{NiO}}/\text{EtOH}$ to avoid the carbon formation as a function of the temperature in the FR, T_{FR} . Four different $\text{H}_2\text{O}/\text{EtOH}$ molar ratios were used (0, 0.5, 1 and 3). A decrease of the temperature allows the use of lower $\text{O}_{\text{NiO}}/\text{EtOH}$ molar ratios to reach the autothermal condition. However, the minimum operating temperature is

fixed by the carbon formation in the process (discontinuous lines in Fig 6). Otherwise, an increase of H_2O avoids carbon formation at lower temperatures, always maintaining autothermal conditions. A $H_2O/EtOH$ of 3 allows working with any $O_{NiO}/EtOH$ molar ratio with no carbon formation at any temperature. However, reaction rates at the operating temperature must be high enough to take place.

3.5 Optimization of H_2 production at a-CLR conditions

Based on the minimum operating temperature obtained previously, the optimization of the a-CLR process was carried out using dehydrated (≈ 100 vol.%), hydrated (95.2 vol.%) and diluted (≈ 52 vol.%) ethanol in the FR, which corresponds to a $H_2O/EtOH$ ratios of 0, 0.2 and 3, respectively.

Fig 7 shows the $O_{NiO}/EtOH$ molar ratio, the variation of enthalpy and the total H_2 production in the global system (a-CLR + WGS + preheaters) for each type of ethanol as a function of the temperature.

A decrease of the T_{FR} implies that a lower $O_{NiO}/EtOH$ molar ratio is required to reach the autothermic process (Fig 7a), which means that H_2 production increases (Fig. 7c) and the surplus energy decreases (Fig. 7b). However, at a specific $O_{NiO}/EtOH$ value there is observed residual methane in the gas composition due to a decrease in the equilibrium constants of the reactions, which implies the presence of a maximum in the H_2 production. This maximum is different based on the amount of H_2O , i.e., it is different for each type of bioethanol. If the dehydrated bioethanol (≈ 100 vol.%) was fed into the FR, the maximum H_2 production would be achieved at 850 °C with 4.5 mol of H_2 per mol of ethanol (number 1 in Fig. 7c). A slight improvement in H_2 production was achieved when hydrated bioethanol was used

(number 2). However, the maximum production was obtained with the diluted bioethanol (≈ 52 vol.% purity), reaching 4.62 mol of H_2 per mol of EtOH at 715 °C in the FR (number 3). It must be considered that external energy must be given in all these cases. To avoid this external energy supply ($\Delta H_G=0$), the operating temperature should be increased (dots 4-5-6 in Fig. 7c), decreasing the H_2 production. However, this fact could be compensated with the energy save in the previous purification of bioethanol [25]. This result opens an important alternative route of H_2 production without CO_2 emissions by using a renewable fuel such as bioethanol.

4. Conclusions

This work shows the operational conditions que maximize the H_2 production in a global system, which is composed by the a-CLR process, preheaters and a water gas shift reactor (WGS), using bioethanol as fuel with no CO_2 emissions to the atmosphere.

In the process pure N_2 is obtained in the AR, due to the amount of oxygen used in the process is controlled by the oxygen fed to the AR. It was determined that it is allowed operating with a wide range of F_s (1.7 – 17 kg/s·MW) with slight variations in the H_2 production, with any NiO content in the OC. It was also demonstrated that its composition is less important than the other variables, always in reasonable limits.

At the same time, the minimum operating temperatures in the FR that allows reaching the a-CLR with no carbon formation (which would imply a decrease of the CO_2 capture efficiency) have been determined for different $H_2O/EtOH$ molar ratios.

With $\text{H}_2\text{O}/\text{EtOH}$ molar ratios higher than 2 – 3 no carbon formation was achieved and the minimum temperature would be limited by kinetic restrictions.

Three different types of bioethanol have been evaluated (dehydrated, hydrated, and diluted). It has been observed that diluted ethanol shows advantages because it maximizes the H_2 production and it allows energy saves in the distillation process (renewable fuel obtaining). It has been determined that it can be obtained 4.62 mol of H_2 per mol of EtOH at T_{FR} equal to 712 °C, considering just the thermodynamic equilibrium (in a real case, it should be considered kinetics aspects as well).

It was also observed that in any case that the H_2 production was maximized external energy supply was required; however, when the diluted ethanol is used, this fact could be compensated with the energy save in the previous purification of bioethanol. This result opens an important alternative route of H_2 production without CO_2 emissions by using a renewable fuel such as bioethanol.

Nomenclature

C_{p_i}	specific heat of each component (kJ/mol·K)
$\text{H}_2\text{O}/\text{EtOH}$	molar ratio of water injected per mol of ethanol fed (-)
F_s	oxygen carrier circulation flow-rate (kg/s)
F_{EtOH}	molar flow of EtOH fed to the FR (mol/s)
$F_{\text{O}_2,\text{in}}$	molar flow of oxygen at the inlet of the AR (mol/s)
$F_{\text{O}_2,\text{out}}$	molar flow of oxygen at the outlet of the AR (mol/s)
$F_{\text{CO}_2,\text{out}}$	molar flow of CO_2 at the outlet of the AR (mol/s)
h_i	enthalpy of each component (kJ/mol)
h_{oi}	standard enthalpy of each component (kJ/mol)

M_{NiO}	molecular weight of NiO (wt.%)
n_i	number of moles of each component (mol)
$O_{NiO}/EtOH$	moles of oxygen transferred by the oxygen carrier to the fuel reactor per mol of ethanol fed
T	operating temperature (°C)
T_{AR}	temperature in the Air reactor (°C)
T_{FR}	temperature in the Fuel reactor (°C)
X_{AR}	conversion of the oxygen carrier at the outlet of the AR
X_{FR}	conversion of the oxygen carrier at the outlet of the FR
$x_{NiO,AR}$	NiO content of the oxygen carrier at the outlet of the AR
$x_{NiO,FR}$	NiO content of the oxygen carrier at the outlet of the FR
$x_{NiO,ox}$	NiO contents of the complete oxidized oxygen carrier $x_{NiO,red}$ NiO contents of the complete reduced oxygen carrier.
ΔH_{AR}	variation of enthalpy inside the FR (kJ/mol EtOH)
ΔH_{CLR}	heat balance in the CLR process (kJ/mol EtOH)
ΔH_{FR}	variation of enthalpy inside the FR (kJ/mol EtOH)
ΔH_G	global heat balance (kJ/mol EtOH)
ΔH_{HE}	variation of enthalpy associated to each heat exchanger (kJ/mol EtOH)
ΔH_{WGS}	variation of enthalpy associated to the WGS reactor. (kJ/mol EtOH)
ΔX_{O_2}	oxygen fed conversion
ΔX_s	the oxygen carrier conversion variation

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Figure Captions

Fig 1. Global H₂ production process with an integrated a-CLR system (blue marked area) using bioethanol. Bioethanol production process (red marked area) was not considered in the balances.

Fig 2. Gas composition in thermodynamic equilibrium as a function of the oxygen reacting in the FR per mol of EtOH. $T_{FR} = 900$ °C. $H_2O/EtOH = 0$ (continuous lines). $H_2O/EtOH = 3$ (discontinuous lines).

Fig 3. Heat and mass balance evaluation as function of $O_{NiO}/EtOH$ molar ratio. a) Heat balance of the CLR system. b) Air reactor temperature. c) Hydrogen production in the global process per mol of bioethanol. Fuel: Pure bioethanol. H_2O addition in the WGS reactor

Fig 4. Effect of the solid circulation in the H₂ production process at autothermal conditions for several NiO contents. a) Solid conversion variation, b) air reactor temperature, c) $O_{NiO}/EtOH$ molar ratio (continuous lines) and H₂ production in the global process (discontinuous lines).

Fig 5. Effect of H_2O addition to the a-CLR system or to the WGS reactor on the H₂ production and AR temperature. Dots represents three different bioethanol purities. $T_{FR} = 900$ °C.

Fig 6. Determination of the operating conditions (T_{FR} and $O_{NiO}/EtOH$) that avoids carbon formation at autothermal conditions for different $H_2O/EtOH$ molar ratios. Continuous lines: $O_{NiO}/EtOH$ molar ratio at autothermal conditions for each FR temperature. Discontinuous lines: minimum $O_{NiO}/EtOH$ that avoids carbon formation.

Fig 7. Effect of the bioethanol purity on the H₂ production as function of the FR temperature. a) Oxygen-to-ethanol molar ratio at autothermal conditions, b) Surplus energy, and c) Total hydrogen production, in the auto-thermal conditions in the CLR system with no carbon formation. Autothermal conditions of the global process (a-CLR + WGS + heat exchangers).

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