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Thermodynamic Analysis of the Absorption Enhanced Autothermal Reforming of Ethanol

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Abstract: *Thermodynamic analysis of the absorption enhanced autothermal reforming of ethanol using CaO as CO_2 absorbent and O_2 in the feed was performed to determine favorable operating conditions to produce a high hydrogen ratio (HR, mols H_2-produced/EtOH-feed) and hydrogen concentration in gas product. Steam/Ethanol (S/EtOH) and oxygen/ethanol (O_2/EtOH) feed molar ratios were varied in order to find autothermal ($\Delta H \approx 0$) and carbon free operating conditions at 300-900°C and CaO as CO_2 absorbent at 1 atm. Carbon formation analysis used S/EtOH = 1.75-2.8, while for hydrogen production varied from stoichiometric; 3:1 to 6.5:1, and O_2/ETOH from 0 to 1.0. Results indicate no carbon formation at S/EtOH ≥ stoichiometric. The absorption enhanced autothermal reforming of ethanol using CaO, O_2/EtOH = 0.33, S/EtOH = 6.5 and 600°C, produced an autothermal system with 98% H_2 and only a reduction of 9.8% in HR and with respect to the CO_2 absorption reforming without O_2 feed.*

Keywords: Absorption-Enhanced-Autothermal-Reforming, CO_2-absorbent, Thermodynamic Analysis.

1. INTRODUCTION

Global warming is a central issue nowadays because its effects on the environment and human condition [1, 2]. Carbon dioxide (CO_2) is one of the main greenhouse gases, and their emissions are primarily produced from the use of fossil fuels for transportation (vehicles) and electricity generation (power plants). Due to this global warming danger and limited supply and rising demand for fossil fuels, alternative energy sources are at present being developed. A sustainable solution to today's energy needs must include the energy generation from renewable sources accompanied with a reduction in both; pollution emissions and a large consumption of raw materials.

Moreover, hydrogen (H_2) is a promising energy vector due to the fact that it can be produced through environmentally friendly processes. For example, biomass and specifically agriculture wastes [3, 4], and water can react to produce hydrogen gas. Hydrogen is an important raw material used in the oil refinery industry and the manufacturing of various chemicals. As energy vector, hydrogen can efficiently be used to generate electricity through electrochemical reactions in fuel cells [5]. Different kinds of fuel cells have been developed, among these the most important are; proton-exchange-membrane fuel cells (PEMFC), solid-oxide fuel cells (SOFC), and molten carbonate fuel cells (MCFC) [5, 6], either for mobile or stationary applications. For hydrogen fuel cells to have a significant impact on reducing greenhouse gas emissions, the hydrogen needs to be produced from renewable sources such as sunlight, either directly or indirectly from biomass through photosynthesis. The use of hydrogen fuel cells in vehicles or in portable power plants will require lightweight H_2 storage or "on-board" reforming of hydrogen-containing compounds into H_2 [7].

Biomass candidates for H_2 production include; sugar, starch, oils, and crop wastes. The production of hydrogen from sugar by catalytic reaction has been demonstrated [8], but the process from glucose so far has shown only 50% selectivity to H_2 and reaction kinetics is extremely slow. Also, a fuel cell operating using sugars

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as raw materials has been demonstrated [9], but the obtained power densities are very low for practical use. Furthermore, biodiesel (the methyl ester of a vegetable oil) can be a good candidate for steam reforming to produce H_2 because the comparable fossil diesel can be reformed [10], although the higher cost of seed oil limits its economics.

On the other hand, ethanol is a very attractive raw material for hydrogen production because of its relatively high hydrogen content, availability, non-toxicity, storage and handling safety. Furthermore, ethanol can be produced renewably by fermentation of biomass sources, such as energy plants, agroindustrial wastes, forestry residue materials, and organic fractions of municipal solid waste. Ethanol produced through these processes constitute what is called bioethanol [11].

Steam reforming of ethanol (SR) for hydrogen production based on the operation-mode can be very different, with important implications on the composition of the reformer effluent and the energy demand, necessary to generate the hydrogen-rich product. These operational modes are: steam-reforming, partial-oxidation and auto-thermal reforming.

Steam-reforming is a highly endothermic process:

$$CH_3CH_2OH + H_2O = CO + 4H_2 \quad \Delta H_R^o = +298 \text{ kJ/mol} \quad (1)$$

Complete steam-reforming (SR) operation is given by the following reaction

$$CH_3CH_2OH + 3H_2O = 2CO_2 + 6H_2 \; \Delta H_R^o = +347 \text{ kJ/mol} \quad (2)$$

while the maximum hydrogen-yield of ethanol steam-reforming can be fixed by 6 moles of H_2/mole ethanol.

Partial-oxidation is the incomplete oxidation of the ethanol feed. This incomplete oxidation generates heat and decomposes the feed to smaller molecules as follows:

$$CH_3CH_2OH+0.5O_2 = 2CO+3H_2 \quad \Delta H_R^o = +57 \text{ kJ mol}^{-1} \quad (3)$$

$$CH_3CH_2OH+O_2 = CO_2+CO+3H_2 \quad \Delta H_R^o = -226 \text{ kJ mol}^{-1} \quad (4)$$

$$CH_3CH_2OH+1.5O_2 = 2CO_2+3H_2 \quad \Delta H_R^o = -509 \text{ kJ mol}^{-1} \quad (5)$$

As the oxygen content in the feed stream is increased, the ethanol is completely oxidized and the maximum heat output is achieved at the expense of an increase in carbon oxides (CO and CO_2) byproducts [12].

Auto-thermal reforming (ATR) is the combination of the above two processes (steam-reforming and partial-oxidation), in order to achieve a minimum energy input necessary to maintain the required reformer temperature. The total reaction of autothermal reforming of ethanol can be written as

$$CH_3CH_2OH+2H_2O+1.5O_2 = 2CO_2+5H_2 \quad \Delta H_R^o = -50 \text{ kJ mol}^{-1} \quad (6)$$

This reaction indicates that the autothermal reforming not only attains thermally sustained operation, but also maximizes hydrogen production [13, 14].

The selection of operating conditions of a reformer depends on various targets. In the case of the ATR operation the temperature is determined at conditions where the heat of the endothermic reforming is compensated with the heat of the exothermic partial oxidation so that the overall reaction heat is approximately null ($\Delta H \approx 0$). Another target of this process is a high hydrogen yield, combined with low carbon oxides (CO and CO_2) content. Maximum hydrogen efficiency and low carbon monoxide content is possible for steam reforming operation. However, steam-reforming is a highly endothermic process and therefore energy demanding. This energy has to be supplied into the system from external sources. In the case of a conventional reforming operation the heat needed to keep the reformer temperature is usually supplied through a furnace where a fossil fuel is burned (typically natural gas) and the fuel demand is intensified during start-up-time. This is unacceptable if renewable hydrogen is to be produced. Therefore the partial-oxidation or auto-thermal operation is preferred as the process is exothermic.

It is inherent to the ATR reforming process that carbon monoxide is generated. The production of carbon monoxide needs to be avoided, as it is an inefficient by-product, which impacts the mass and size of the fuel processor (WGS). Furthermore, the production of carbon dioxide is also promoted under this operation scheme and both oxides represent two additional separate processes to obtain a high purity hydrogen product. On one hand, in a fuel processing system the reformer is followed by two water gas shift (WGS) reactors to reduce the carbon monoxide contents to the desired level. On the other hand, carbon dioxide is eliminated from the effluent stream of the WGS by an amine absorption process or a PSA unit to finally generate a high purity hydrogen stream, typically 99.9%. Even though there are some disadvantages of this operation mode ATR is considered to be the most energetically efficient and cost-effective reforming method [15, 16].

Another reforming operating mode, developed in the last decade deals with a modification of the conventional reforming process. This alternate processes was called the absorption enhanced reforming (AER). This AER process provides a promising alternative for a single step high purity hydrogen production [17]. The fundamental concept in which this process is based is the Le Chatellier's principle where the reforming equilibrium can be shifted towards the production of hydrogen when CO_2 is removed *in situ* within the reactor. Thus if the carbon dioxide generated during the steam reforming step is removed from the gas phase using a solid CO_2 absorbent such as CaO the hydrogen production will be enhanced. In the AER reactor a mixture of a CO_2 absorbent (for example CaO) and a reforming catalyst will theoretically produce a high purity hydrogen stream in one single step. The combination of the CO_2 absorption by CaO through the reaction:

$$CaO + CO_2(g) = CaCO_3 \quad \Delta H^\circ_{298} = -178.3 \text{ kJ/mol} \quad (7)$$

and the steam reforming of ethanol lead to the following reaction

$$C_2H_6O(g) + 3H_2O(g) + 2CaO = 2CaCO_3 + 6H_2(g) \quad \Delta H^\circ_{298} = -185.3 \text{ kJ/mol} \quad (8)$$

When comparing equation (2) with equation (8), it is evident that the use of a CO_2 absorbent changed from an endothermic steam reforming reaction to an exothermic reaction, which implies potential energy savings with the use of a solid CO_2 absorbent. However, this absorbent must be regenerated if a continuous process is desired and then the high endothermic reverse reaction (7) will eventually be required to be performed.

Thermodynamic analyses and experimental studies related to the use of simultaneous CO_2 removal using CaO as absorbent combined with the steam reforming of ethanol for hydrogen production has been reported by several authors [17, 18]. However, the balance between the high endothermic ethanol reforming reaction (2) and the high exothermic carbonation reaction (7) for autothermal operation ($\Delta H_R \approx 0$) requires operating temperatures of less than 380°C (S/EtOH = 6 and CaO/EtOH = 2.5 molar ratios). At these conditions the overall reaction rate is rather slow and consequently of not practical interest. At ethanol AER optimal operating temperatures (600-700ºC) hydrogen production is enhanced generating a high purity H_2 stream accompanied with a moderate endothermic overall heat of reaction. Therefore, there is a need of supplemental heat for the AER reactor to be able to operate at autothermal conditions where reaction temperatures (600-700ºC) are reported to generate sufficiently fast reactions kinetics [14].

From the above reforming operating modes studied in the past is then convenient to take advantage of the AER process scheme, which presumably produce high hydrogen yield and content combined with a moderate endothermic reaction heat at temperatures of interest (600-700ºC) and the ATR process scheme that is able to supply the necessary heat required for the AER process to operate in an autothermal mode ($\Delta H_R \approx 0$). Therefore, in the present thermodynamic study the combination of the ethanol reforming reaction (2), CO_2 absorption reaction by CaO (7) and ethanol partial oxidation reactions (3) to (5) are proposed as a renewable and energy efficient (autothermal operation) reforming mode of operation (AER-ATR) to produce a high H_2 content product gas in one single step.

Therefore, the objective of the present study is to perform a thermodynamic analysis of the AER-ATR process to determine carbon free and favorable operating conditions to produce a high purity hydrogen stream. The influence of steam-to-ethanol (S/EtOH) and oxygen-to-ethanol (O_2/EtOH) feed molar ratios and temperature on the product gas concentration were investigated at atmospheric conditions. These results were then compared to the ethanol steam reforming (ESR) and AER reforming modes. Results will be compared with experimental (where available) and theoretical data generated and found in existing literature. Furthermore, it is expected that during the steam reforming of ethanol, carbon deposition over catalysts may be the main cause for deactivation, resulting in catalyst low durability and activity loss. Therefore, additionally a study of conditions where this carbon deposition is expected under the AER-ATR process was included and compared with current reforming operating modes. Hence, S/EtOH and O_2/EtOH feed ratios were varied in order to find autothermal reaction conditions ($\Delta H \approx 0$) and carbon free operating regions. Equilibrium product compositions were studied from 300-900°C and CaO was employed as CO_2 absorbent at 1 atm. Carbon formation analysis used S/EtOH from 1.75-2.8, while for hydrogen production was varied from stoichiometric; 3:1 to 6.5:1, and O_2/ETOH from 0 to 1.0.

2. SIMULATION CALCULATIONS

2.1. Gibbs free energy minimization technique

In a reaction system where many simultaneous reactions take place, equilibrium calculations can be performed through the Gibbs energy minimization approach (also called the non-stoichiometric method). In this technique the total free energy of the system consisting of an ideal gas phase and pure condensed phases, can be expressed as:

$$\frac{G}{RT} = \left(\sum_{i=1}^{N} n_i \frac{G^\circ_i}{RT} + \ln(y_i P) \right)_{gas} + \frac{1}{RT} \left(\sum_{i=1}^{N} n_i G^\circ_i \right)_{condensed} \tag{9}$$

The technique is based in finding different values of n_i which minimizes the objective function (7) and are subjected to the constraints of the elemental mass balance:

$$\sum_{i=1}^{N} a_{ij} n_i = A_j, j = 1, 2, 3 ..., k \tag{10}$$

where a_{ij} is the number of atoms of the j^{th} element in a mole of the i^{th} species. A_j is defined as the total number of atoms of the j^{th} element in the reaction mixture [19]. All calculations were performed through the use of the equilibrium module of the HSC chemistry software for windows [20]. HSC calculates the equilibrium composition of all possible combination of reactions that are able to take place within the thermodynamic system. These equilibrium calculations make use of the equilibrium composition module of the HSC program that is based on the Gibbs free energy minimization technique. The GIBBS program of this module finds the most stable phase combination and seeks the phase compositions where the Gibbs free energy of the system reaches its minimum (equation 9) at a fixed mass balance (a constraint minimization problem, equation 10), constant pressure and temperature.

In this non-stoichiometric approach every species in the system must be defined. The selection of feasible products should be based on previous experimental results found in the literature. For each system the possible species are specified based on reported experimental and thermodynamic analysis studies. In the steam reforming systems studied the species included were: ethanol, ethylene, ethane, acetone, acetaldehyde, acetic acid, C, CO, CH_4, CO_2, H_2, H_2O, CaO and $CaCO_3$. These were based on reported experimental species found in the literature [21-23].

3. RESULTS AND DISCUSSION

3.1. Thermodynamically possible products

During the equilibrium calculations the HSC program requires the input of all possible chemical species present in the system as reactants and products. For the steam reforming system the species considered at equilibrium were all gaseous and solid species already described in section 2.1 and those found in the current literature that appear when ethanol is converted along with other intermediate oxygenated hydrocarbons. Specifically, for the ethanol reforming system the additional intermediate species considered were: ethylene, ethane, acetaldehyde, acetic acid and acetone [17, 18, 24-26]. In practice, alcohol steam reforming reactions are under kinetic control, where suitable catalysts and supports are able to completely convert all the biofuel to avoid intermediate products. All this agrees well with the fact that only trace amounts (less than 1ppm) of these oxygenated intermediates were found in all the thermodynamic calculations performed and therefore these were not reported in the present study.

3.2. Carbon formation

Figure 1 shows the effect of steam to ethanol (S/EtOH) molar ratios from 0-2.8 and temperature from 300-900ºC on the number of moles of carbon (graphite) produced / kmol of Ethanol feed (1kmol) through the steam reforming (SR) and the absorption en-

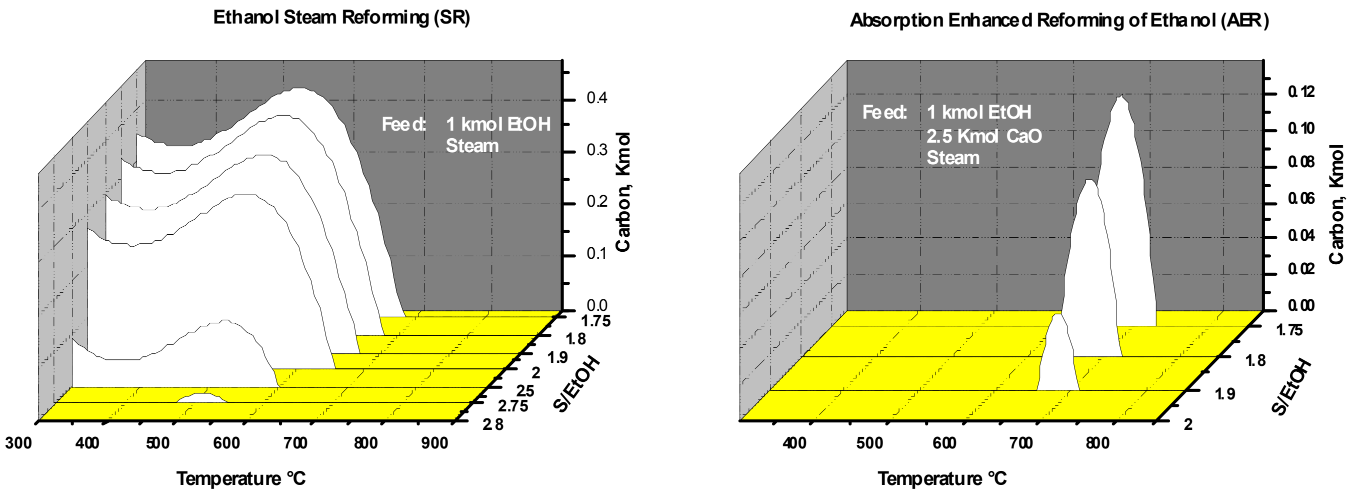

Figure 1. Carbon formation for the SR and AER processes as a function of T and S/EtOH ratio.

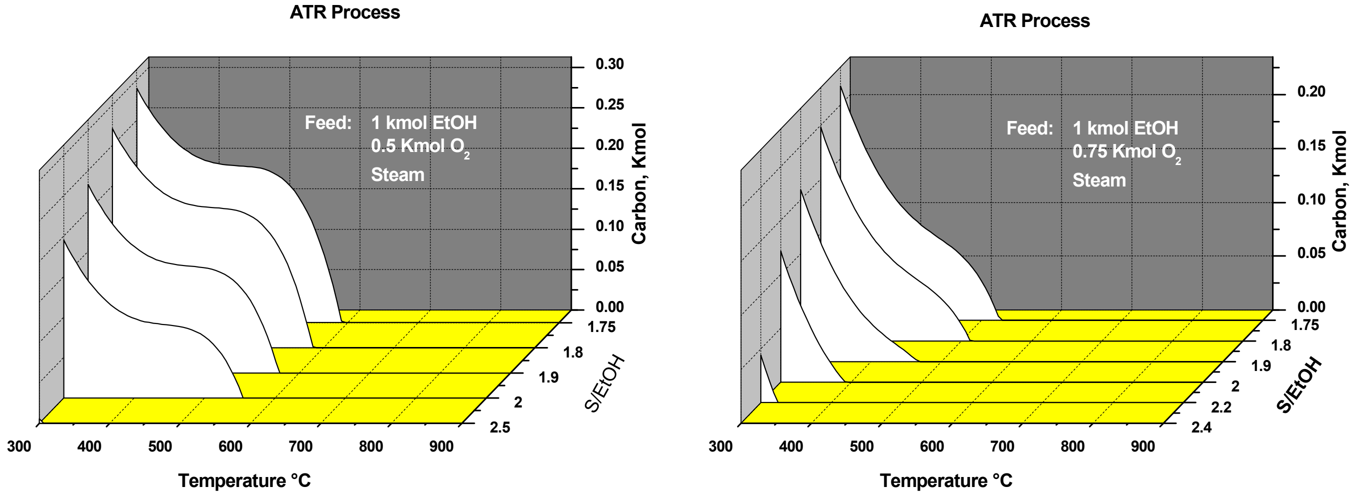

Figure 2. Carbon formation for the ATR process at O_2/EtOH ratios of0.5 and 0.75 as a function of T and S/EtOH ratios.

hanced reforming of ethanol processes.

For the SR process 1 Kmol of ethanol was fed to the reaction system and the corresponding steam for each S/EtOH ratio, while for the AER system 2.5 Kmol of CaO was also fed along with steam and ethanol.

In these plots is evident that without the use of a CO_2 absorbent carbon formation is favored and its maximum is reached at lower temperatures ($T < 700°C$) than with the use of an absorbent ($600 < T < 750°C$) . The SR produced a maximum carbon formation of 0.43 kmol per mol of ethanol fed to the system at S/EtOH ratio of 1.75 and it is found at a temperature of 536°C. Greater temperatures and S/EtOH ratios will produce lower amounts of carbon and at S/EtOH ratio greater than 2.75 and higher temperatures will secure a carbon free operation region under this system. Whereas, under the AER system carbon formation is only formed at high temperatures and in the range from 600-750ºC and from S/EtOH ratios from 0-1.9, with a maximum carbon formation of 0.128 kmol/kmol EtOH fed at a S/EtOH ratio of 1.75 and 686ºC. Higher S/EtOH ratios than 1.9 will ensure a carbon free operation under this reaction system. From Figure 1 it is clear that the use of a CO_2 absorbent inhibits carbon formation in about three orders of magnitude and smaller S/EtOH ratios can be used without the formation of carbon in the reaction system.

The behavior related to the lower carbon formation found with the use of a CO_2 absorbent (very low risk of carbon formation), is directly related to the reduction in CO content. Li [25] reported in his thermodynamic study, that graphite formation is suppressed with CO_2 absorption. According to this author, the Boudouard reaction:

$$2CO(g) = CO_2(g) + C(s) \quad \Delta H°298 = -172.5 \text{ kJ/mol} \qquad (11)$$

is shifted towards the reverse Boudouard reaction because its equilibrium constant is related to the square of CO concentration.

Figure 2 presents results of equilibrium calculations for the ATR

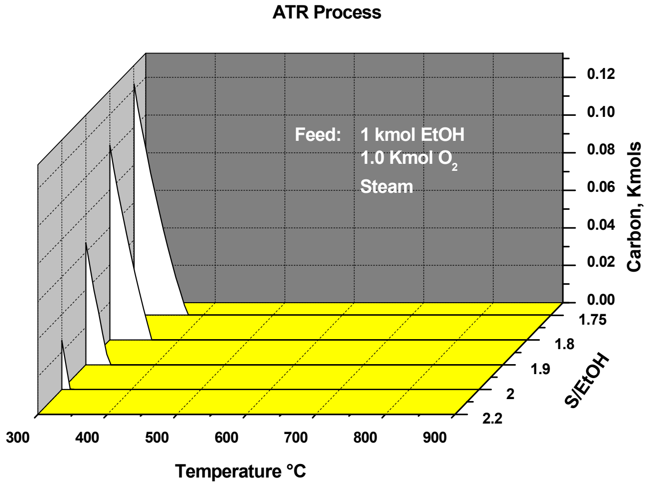

Figure 3. Carbon formation for the ATR process at O_2/EtOH = 1.0 as a function of T and S/EtOH.

reforming mode of ethanol. In this plot the carbon formation in kmol as a function of S/EtOH and temperature are presented using two different O_2 feed levels; O_2/EtOH ratios of 0.5 and 0.75, respectively.

From this Figure it can be seen that at O_2/EtOH = 0.5 carbon formation is predicted at a low temperature range of 300-600ºC and S/EtOH < 2 within the ATR system as high as 0.28 kmol at 300ºC. Greater temperatures from this region will prevent carbon to be formed in this reaction system. However, if the O_2 content is increased to a level of O_2/EtOH = 0.75 this will produce a reduction of the carbon formation region accompanied with lower temperatures at higher S/EtOH ratios. Maximum temperature for carbon formation was reduced to 524ºC and S/EtOH = 1.75. This effect implies that at values of S/EtOH higher than 2.2 will ensure a carbon free operation. A further increase in the O_2 content for the ATR process can be seen in Figure 3, where the O_2 content in the feed is increased to a level of O_2/EtOH = 1.0. Here, the carbon formation region is additionally reduced with smaller regions for carbon deposition (T < 400°C) and as the S/EtOH is increased to values greater than 2.0 this will prevent carbon formation at all studied temperatures.

This behavior can be explained in terms of the following coke gasification reactions:

$$O_2 + C(s) = CO_2 \quad \Delta H°298 = -393.48 \text{ kJ/mol} \tag{12}$$

$$\tfrac{1}{2} O_2 + C(s) = CO \quad \Delta H°298 = -110.70 \text{ kJ/mol} \tag{13}$$

The gasification equilibrium is also dependent on the steam to EtOH ratio and the temperature of the system. For instance, at S/EtOH ratios of 2 and greater, carbon is completely gasified at temperatures of 400°C and greater. This behavior can also be seen when the equilibrium content of carbon oxides are carefully examined. As the O_2 content in the feed is increased the equilibrium content of the carbon oxides (CO and CO_2) are also increased (not shown in Figures), which is consistent with the promotion of reaction (12) and (13). In reaction (12), oxygen fully gasifies carbon to CO_2 at an O_2/EtOH = 1.0 and, when there is insufficient oxygen O_2/EtOH < 0.5, gasification to CO is thermodynamically favorable at temperatures above 500°C. Nevertheless, carbon formation apart from reaction (11) can also be generated through the following reactions:

$$CH_4 = C(s) + 2H_2 \quad \Delta H°298 = +73.84 \text{ kJ/mol} \tag{14}$$

$$CO + H_2 = C(s) + H_2O \quad \Delta H°298 = -130.8 \text{ kJ/mol} \tag{15}$$

$$CO_2 + 2H_2 = C(s) + 2H_2O \quad \Delta H°298 = -89.6 \text{ kJ/mol} \tag{16}$$

Therefore, there is a complex network of reactions involved in the entire process. However the main fact is that O_2 content in the feed through the ATR process scheme produces a reduction in the carbon formation through gasification reactions (12) and (13).

Figure 4 shows the carbon formation as a function of S/EtOH and temperature for the AER-ATR reaction system at O_2/EtOH of 0.1 and 0.25, respectively. Feed to each system consisted in 1 kmol

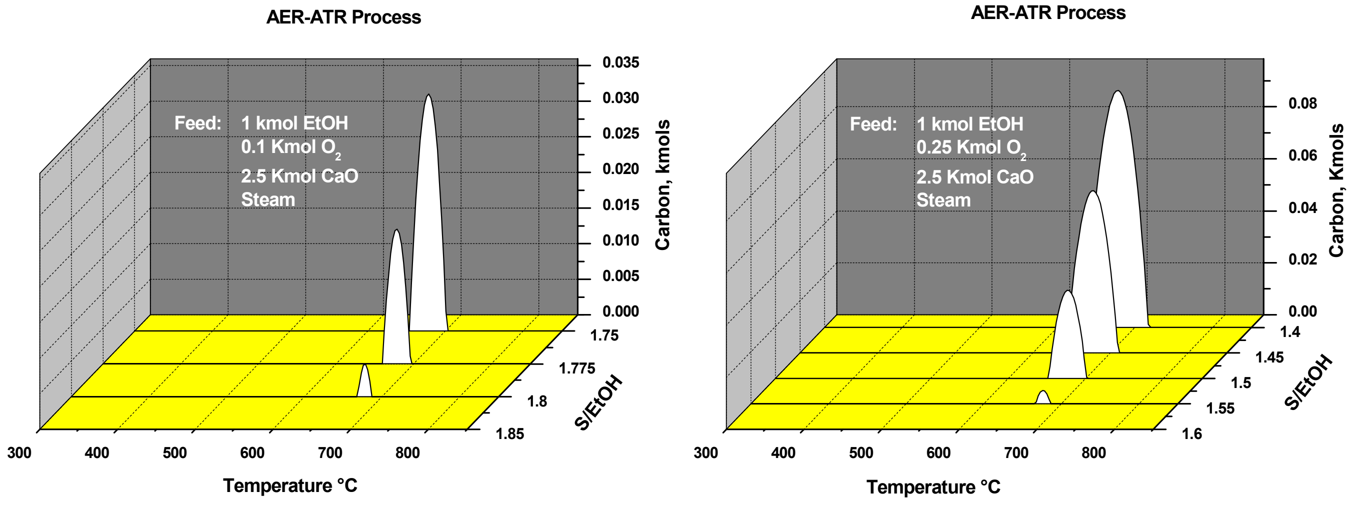

Figure 4. Carbon formation for the AER-ATR process at O_2/EtOH = 0.1 and 0.25 as a function of T and S/EtOH.

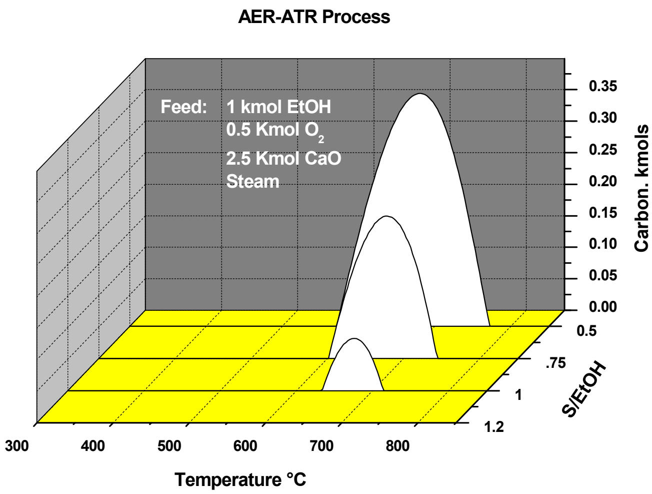

Figure 5. Carbon formation for the AER-ATR process at O_2/EtOH = 0.5 and 0.25 as a function of T and S/EtOH.

of ethanol, 2.5 kmol of CaO and the corresponding amount of steam for each S/EtOH ratio. For the case of O_2/EtOH = 0.1 the S/EtOH ratio was varied from 0 to 1.85, while for O_2/EtOH = 0.25 this changed from 0 to 1.6.

Here it can be seen that the effect of combining the AER and the ATR reforming modes resulted in carbon free regions located at lower S/EtOH ratios. For example at O_2/EtOH = 0.1 and 0.25 S/EtOH ratios as low as 1.85 and 1.6, can be operated without any carbon formation, respectively. However, one particular feature in Figure 4 is that carbon formation is now promoted at high temperatures (650 -800°C). This behavior can be explained in terms of reaction (14), where the production of CH_4 is favored at small S/EtOH ratios and then this is presumably converted to carbon. This behavior is even more enhanced as the S/EtOH is further reduced as can be seen in Figure 4.

Finally Figure 5 presents results at O_2/EtOH = 0.5 under the AER-ATR reforming mode. Here it can be seen that even though the amount of carbon is increased this is only at S/EtOH ratios of less than 1.2.

Here the increase in O_2 content within the absorption enhanced reforming of ethanol caused that the lower limit for carbon formation in terms of S/EtOH to be reduced. When comparing the SR, AER, ATR and AER-ATR it can be found that the amount of steam employed for the AER-ATR process is about half with respect to the S/EtOH ratio needed to avoid carbon formation. Furthermore, in the case of the AER-ATR process, higher temperatures than 600°C are needed for carbon to be formed being these not typically found in a conventional reforming operation. Therefore, it can be concluded that in all the reforming operating modes (SR, AER, ATR and AER-ATR) greater than stoichiometric values will secure a carbon free operation. And in terms of the order from higher to lower carbon formation is: SR > ATR > AER > AER-ATR.

3.3. Thermoneutral condition

In an autothermal steam reforming process, oxygen supplies the necessary heat via the oxidation reaction for the endothermic steam reforming; increasing oxygen to ethanol molar ratio (O_2/EtOH) decreases an external heat requirement. As a result, it is possible to operate the autothermal reformer without supplying external heat input by controlling appropriate oxygen feed ratios. This condition is referred as a thermoneutral condition ($\Delta H \approx 0$). The operating temperature at which the external heat flow equals to zero is also known as an adiabatic temperature. Table 1 shows the behavior of the adiabatic temperature and O_2/EtOH ratio at different S/EtOH ratios. Also in this table the different reforming modes are presented (SR, ATR, AER and AER-ATR) as well as the equilibrium dry molar composition of the gas product and the total kmols of hydrogen produced at each condition studied.

Table 1. Adiabatic temperature and O_2/EtOH ratio at different S/EtOH ratios.

FEED, kmols		S/EtOH	Adiabatic T ($\Delta H = 0$)	Product Composition % mol				H_2	FEED, kmols		S/EtOH	Adiabatic T ($\Delta H = 0$)	Product Composition % mol				H_2
CaO	O_2	Molar Ratio	(°C)	H_2	CO	CO_2	CH_4	kmols	CaO	O_2	Molar Ratio	(°C)	H_2	CO	CO_2	CH_4	kmols
-	-	3	334	13.4	0.1	25.0	61.5	0.3	2.5	-	3	481	90.8	0.0	0.0	9.2	4.3
-	-	6.5	$\Delta H > 0$	71.7	8.1	19.4	2.8	4.7	2.5	-	6.5	372	98.3	~ 0	~ 0	1.7	5.6
-	0.1	3	312	18.0	0.1	27.0	54.9	0.4	2.5	0.1	3	572	97.8	0.5	0.3	7.4	4.4
-	0.1	6.5	403	27.3	0.6	26.4	45.7	2.7	2.5	0.1	6.5	457	98.6	0.0	0.0	1.3	5.5
-	0.25	3	475	42.5	2.5	26.7	28.3	1.5	2.5	0.25	3	639	90.7	3.4	1.7	4.2	4.5
-	0.25	6.5	390	36.7	0.4	28.6	34.2	1.2	2.5	0.25	6.5	566	98.2	0.3	0.7	0.8	5.3
-	-	-	-	-	-	-	-	-	2.5	0.3	3	651	90.1	4.4	2.2	3.3	4.5
-	-	-	-	-	-	-	-	-	2.5	0.3	6.5	590	97.5	0.6	1.3	0.6	5.2
-	-	-	-	-	-	-	-	-	2.5	0.4	3	675	88.3	6.5	3.4	1.9	4.5
-	-	-	-	-	-	-	-	-	2.5	0.4	6.5	627	94.8	1.6	3.4	0.4	5.1
-	1	3	$\Delta H < 0$	59.2	10.9	27.0	2.9	2.9	-	-	-	-	-	-	-	-	-
-	1	6.5	718	63.1	10.3	26.5	0.0	3.4	-	-	-	-	-	-	-	-	-

In this Table two levels of S/EtOH ratios were explored; 3 (stoichiometric condition) and 6.5. Intermediate values were also calculated but only these were reported for simplicity reasons. In Table 1 autothermal conditions for the SR process at S/EtOH = 3 reports an autothermal temperature of 334°C accompanied with a very poor hydrogen production (0.3 kmol) and purity (13.4%). This was expected since the reaction system is very endothermic at stoichiometric conditions and this was the case for the S/EtOH = 6.5, since from a temperature range from 300-900 ºC an adiabatic temperature was not found even though the hydrogen content was increased (4.7 kmols) and its purity (71.7%) with mayor impurities being CO and CO_2. In the same Table the ATR reforming mode was also explored in terms of the autothermal condition. Here, different O_2/EtOH ratios were studied; 0.1, 0.25, 0.375, 0.5, 0.75, 0.85 and 1.0. Generally, in terms of the adiabatic temperature as the S/EtOH ratio was increased the adiabatic temperature was reduced.

These results imply that the net energy required from the reactions grows when the excess steam is fed to the reaction system. At O_2/EtOH = 0.1 and S/EtOH = 3.0 results in an adiabatic temperature of 312°C, which produces very small hydrogen product and purity. Furthermore, this condition is not kinetically feasible for practical purposes. Therefore, an increase in the O_2 content was explored and this was reflected in a gradual increase in the adiabatic temperature as well as the hydrogen content and purity. For example, at O_2/EtOH = 0.25 and 1.0 with S/EtOH = 6.5 temperatures of 390 and 718°C were found with hydrogen contents of 1.2 and 3.4 kmols, and H_2 purities of 42 and 63% respectively. As the oxygen content was increased the concentrations of carbon oxides (CO and CO_2) were also increased, since ethanol partial oxidation reactions (3) to (5) are promoted with higher oxygen content and temperatures. Methane concentrations decreased due to the enhancement of the methane reforming reaction at high temperatures. Therefore, even the autothermal condition produced lower hydrogen content with respect to the SR operating mode at expense of an adiabatic reactor operation. These results are consistent with studies reported by several authors in the literature [14, 19, 27, 28].

Also, in Table 1 the AER process was evaluated in terms of the adiabatic condition for a possible autothermal operation. In this Table 2.5 kmols of CaO were used at S/EtOH of 3 and 6.5 and adiabatic temperatures were 481 and 372°C, respectively. These results generated hydrogen contents and purities of 4.3 and 5.6 kmols and 90.8 and 98.3%, respectively. Clearly, these are not the optimum thermodynamic operating conditions for a maximum hydrogen production that so far have been reported in the literature which are: A feed of 2.5 kmol CaO, S/EtOH = 6.5, 634°C, and 5.7 kmol of hydrogen being produced [29]. However, these conditions are moderately endothermic with a ΔH_R = + 196.5 kJ/kmol. The values reported in Table 1 for the autothermal condition under the AER process are still at temperatures (372 - 481°C) where the ethanol reforming reaction are kinetically limited and the hydrogen content may necessarily be reduced (3.4 - 4.3 kmols of H_2) at the expense of an adiabatic operating temperature. Therefore, the need of additional heat to be supplied to the AER reactor is expected to be included in a possible continuous operation of this process.

On the other hand, Table 1also presents results of the AER-ATR operating mode process proposed in the present work. Here, different O_2/EtOH ratios were studied; 0.1, 0.2, 0.25, 0.3, 0.35 and 0.4. In terms of the adiabatic temperature here also as the S/EtOH ratio was increased the adiabatic temperature was reduced. At O_2/EtOH = 0.1 and S/EtOH = 3.0 results indicate an adiabatic temperature of 572°C, producing a hydrogen product and purity of 4.4 kmols and 97.8%, respectively. Major impurity of this product gas consisted of methane with 7.4% accompanied with fractional percentages of carbon oxides (CO and CO_2). As the S/EtOH increased to a value of 6.5, this even further enhanced the hydrogen production to 5.5 kmols and 98.6% with a consequent decrease in the adiabatic temperature to a value of 457°C. A further increase in the oxygen content to a O_2/EtOH = 0.3 and S/EtOH = 3.0 generated an adiabatic temperature of 651°C which is close to the typical reforming temperature of a catalytic autothermal steam reforming of ethanol reported by Deluga et al. [14]. They experimentally found that catalytic conversion of ethanol was only 40% at 400°C but rose to above 95% by 650°C. At 400°C, acetaldehyde and CH_4 selectivities were 16 and 14%, respectively, for a total selectivity to undesired minor byproducts of about 30%. Both of these species decreased with increasing temperature and acetaldehyde fell to a negligible level by 650°C. In their studies, they concluded that ethanol conversion was lower and minor byproducts were more abundant at lower temperatures, indicating that catalyst temperatures above 600°C are needed for optimum performance.

A further increase in S/EtOH to 6.5 still at O_2/EtOH = 0.3 and using CaO as a CO_2 absorbent in the reaction system, generated a hydrogen product of 5.2 kmols and 97.5% purity with a consequent decrease in the adiabatic temperature to a value of 590°C. Again, mayor impurities were methane and carbon oxides. This adiabatic temperature value is close the desired catalytic operating temperatures experimentally found by Deluga et al [14]. A further increase in oxygen content to a value of O_2/EtOH = 0.4 and S/EtOH ratio of 6.5 generated an adiabatic temperature of 627°C accompanied with a reduction in the hydrogen content and purity of 5.1 kmols and 94.8%, respectively. This behavior can be explained in terms of an increase of the carbon oxides content (CO and CO_2) that presumably promote the ethanol partial oxidation reactions thus producing gaseous carbon species that eventually generate a slight reduction in the hydrogen being produced. Therefore, it can be concluded that optimal operating conditions for high hydrogen production and purity in the AER-ATR process are given by an O_2/EtOH range of 0.3-0.4, S/EtOH = 6.5 and an adiabatic temperature range of 590-627°C.

Figure 6 shows autothermal thermodynamic equilibrium results for the AER-ATR system where several graphs present the dry product gas composition of H_2, CO, CO_2 and CH_4 and these are plotted as a function of temperature (300-900°C) and S/EtOH for an O_2/EtOH = 0.35 and 2.5 kmol of CaO feed. Here in these Figures it is evident the effect of the S/EtOH ratio and temperature in order to achieve a hydrogen product gas of 97.5% purity at 590°C accompanied with very small amount of gas impurities. The mayor impurity at these conditions is due to methane formation. However, in practical applications this may not be kinetically feasible, especially at reactor conditions where permanent gas displacement takes place (continuous flow reactors), since thermodynamic calculations in the present analysis consider a batch reactor system as a basis for the equilibrium calculations (Gibbs free energy minimization technique).

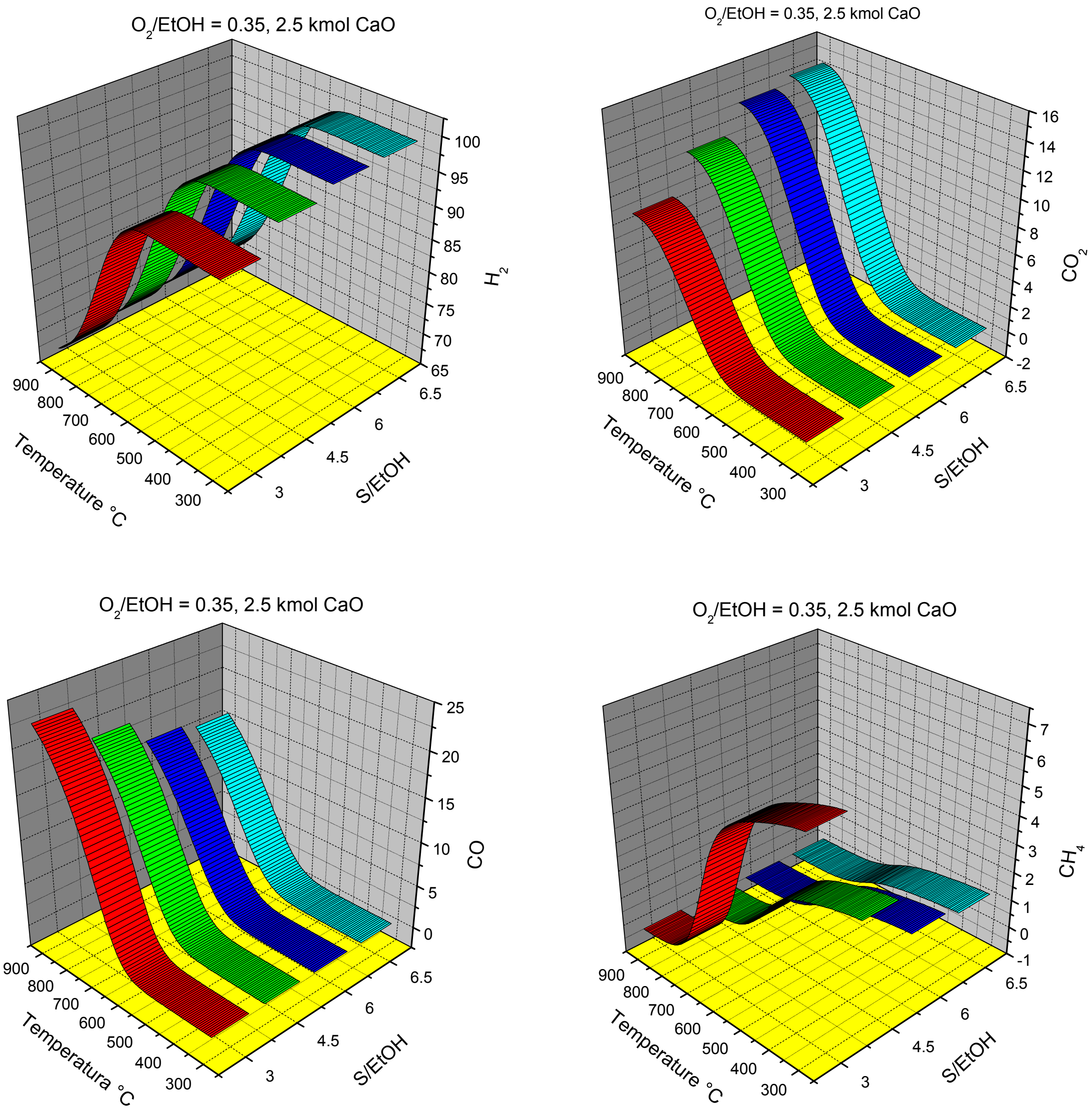

Figure 6. AER-ATR product equilibrium compositions as a function of T and S/EtOH at O_2/EtOH = 0.35 and 2.5 kmol CaO feed.

4. CONCLUSIONS

Thermodynamic analysis of steam reforming of ethanol through SR, ATR, AER and AER-ATR reforming process schemes were carried out to determine favorable operating conditions to produce a high purity H_2 gas product. Results indicate no carbon formation at steam to ethanol ratios less than stoichiometric values (S/EtOH $\leq$ 3, stoichiometric) for the corresponding steam reforming reactions. In the SR process greater temperatures than 536°C and S/EtOH ratios greater than 2.75 will secure a carbon free operation under this system. Whereas, under the AER system carbon formation can be avoided with S/EtOH ratios greater than 1.9 and 686ºC combined with CaO as a solid CO_2 absorbent. The use of a CO_2 absorbent inhibits carbon formation in about three orders of magnitude with respect to the SR process. In the ATR process S/EtOH higher than 2.0 will guarantee a carbon free operation at O_2 content in the feed in the order of O_2/EtOH = 1.0 and temperatures lower than 400°C. In the case of the AER-ATR process at oxygen contents of about O_2/EtOH = 0.5, S/EtOH ratios greater than 1.2 are needed in order to warrant a carbon free operation at all temperatures studied. In all the reforming operating modes (SR, AER, ATR and AER-ATR) greater than stoichiometric values will secure carbon free operation. In terms of the order from higher to lower carbon formation is: SR > ATR > AER > AER-ATR. Finally, optimal operating conditions for high hydrogen production and purity in the AER-ATR process are given by an O_2/EtOH range of 0.3-0.4, S/EtOH = 6.5 and an adiabatic temperature range from 590-627°C.

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