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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<sub>2</sub> absorbent was performed to determine favorable operating conditions to produce a high hydrogen ratio (HR, mols H<sub>2</sub>-produced/EtOH-feed) and hydrogen concentration in gas product. Steam/Ethanol and oxygen/ethanol 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, steam to ethanol molar feed ratio (S/EtOH), oxygen to EtOH ratio (O<sub>2</sub>/EtOH) and CaO as CO<sub>2</sub> 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<sub>2</sub>/ETOH from 0 to 1.0. Results indicate no carbon formation at S/EtOH  $\geq$  stoichiometric. Conventional ethanol reforming at T = 600°C and S/EtOH = 6.5 resulted in a HR of 4.7 and a highly endothermic system. The introduction of O<sub>2</sub> (ATR) in the feed (O<sub>2</sub>/EtOH = 0.88) produced a reduction in HR of 22% at autothermal conditions with no carbon formation, while the use of a CO<sub>2</sub> absorbent (CaO) combined with conventional reforming resulted in an increase in H<sub>2</sub> purity and HPR of about 21% with a still endothermic system. Whereas, the absorption enhanced autothermal reforming of ethanol using CaO, O<sub>2</sub>/EtOH = 0.33, S/EtOH = 6.5 and 600°C, produced an autothermal system with 98% H<sub>2</sub> content and only a reduction of 9.8% in HR and with respect to the CO<sub>2</sub> absorption reforming without O<sub>2</sub> as a feed. Higher O<sub>2</sub>/EtOH values than 0.33 produced a significant reduction in hydrogen content and purity at equilibrium.

**Keywords:** Absorption-Enhanced-Autothermal-Reforming, CO<sub>2</sub>-absorbent, Thermodynamic Analysis

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## **1. INTRODUCTION**

Global warming is a central issue nowadays because its effects on the environment and human condition [1, 2]. Carbon dioxide ( $\text{CO}_2$ ) is one of the main greenhouse gases, and  $\text{CO}_2$  emissions are produced primarily 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.

Hydrogen ( $\text{H}_2$ ) 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  $\text{H}_2$  storage or “on-board” reforming of hydrogen-containing compounds into  $\text{H}_2$  [7].

Biomass candidates for  $\text{H}_2$  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  $\text{H}_2$  and reaction kinetics is extremely slow. Also, a fuel cell operating using sugars 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  $\text{H}_2$  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, and 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 is called bioethanol [11].



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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 highly endothermic process:



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



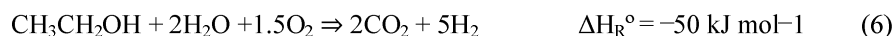
while the maximum hydrogen-yield of ethanol steam-reforming can be fixed by 6 moles of  $\text{H}_2$ /mole ethanol.

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



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 ( $\text{CO}$  and  $\text{CO}_2$ ) subproducts [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



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

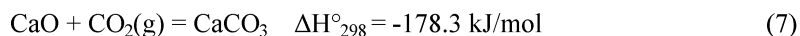
The selection of operating conditions of a reformer is depending on various targets. In the case of the ATR operation the temperature is determined at conditions where the heat of the endothermic reforming is compensated with the heat of the exothermic partial oxidation so that the overall reaction heat is approximately null ( $\Delta H \approx 0$ ). Another target of this process is a high hydrogen yield, combined with low carbon oxides ( $\text{CO}$  and  $\text{CO}_2$ ) 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

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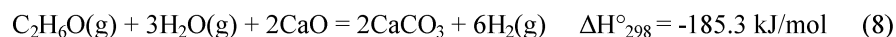
demand is intensified during start-up-time. This is unacceptable if renewable hydrogen is to be produced. Therefore the partial-oxidation or auto-thermal operation is preferred as the process is exothermic.

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<sub>2</sub> 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<sub>2</sub> absorbent such as CaO the hydrogen production will be enhanced. In the AER reactor a mixture of a CO<sub>2</sub> 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<sub>2</sub> absorption by CaO through the reaction:



and the steam reforming of ethanol lead to the following reaction



When comparing equation (2) with equation (8), it is evident that the use of a CO<sub>2</sub> absorbent changed from an endothermic steam reforming reaction to an exothermic reaction, which implies potential energy savings with the use of a solid CO<sub>2</sub> 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.

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Thermodynamic analyses and experimental studies related to the use of simultaneous CO<sub>2</sub> 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 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 (600-700°C) hydrogen production is enhanced generating a high purity H<sub>2</sub> 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 (600-700°C) are reported to generate sufficiently fast reactions kinetics [19].

From the above modes of reforming operations 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 (600-700°C) and the ATR process scheme that is able 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>/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 (EST) 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 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<sub>2</sub>/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<sub>2</sub> 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<sub>2</sub>/EtOH from 0 to 1.0.

## 2. SIMULATION CALCULATIONS

### 2.1 Gibbs Free Energy Minimization Technique



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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:

$$G = \sum_i n_i \mu_i$$

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:

where  $a_{ij}$  is the number of atoms of the  $j^{\text{th}}$  element in a mole of the  $i^{\text{th}}$  species.  $A_j$  is defined as the total number of atoms of the  $j^{\text{th}}$  element in the reaction mixture [20]. All calculations were performed through the use of the equilibrium module of the HSC chemistry software for windows [21]. 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<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, CaO and CaCO<sub>3</sub>. These were based on reported experimental species found in the literature [22-24].

### 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, 25-27]. 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 show the effect of steam to ethanol (S/EtOH) molar ratios from 0-2.8 and temperature from 300-900°C on the number of moles of carbon (graphite) produced / kmol of Ethanol feed (1Kmol) through the steam reforming (SR) and the absorption enhanced reforming of ethanol processes.

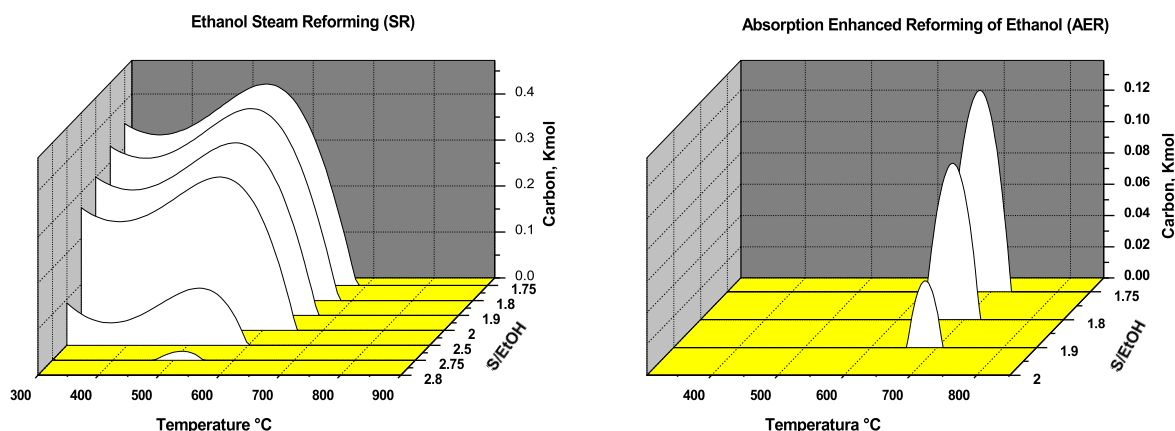


Figure 1. Carbon Formation for the SR and AER processes as a function of T and S/EtOH ratio

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<sub>2</sub> absorbent carbon formation is favored and its maximum is reached at lower temperatures ( $T < 700^{\circ}\text{C}$ ) than with the use of an absorbent ( $600 < T < 750^{\circ}\text{C}$ ). 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 temperatures higher will insure a carbon free operation under this system. Whereas, under the AER system carbon formation is only formed at high temperatures and in the range from 600-750°C 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 686°C. 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<sub>2</sub> 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.

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The behavior related to the lower carbon formation found with the use of a CO<sub>2</sub> absorbent (very low risk of carbon formation), is directly related to the reduction in CO content. Li [28] reported in his thermodynamic study, that graphite formation is suppressed with CO<sub>2</sub> absorption. According to this author, the Boudouard reaction:



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 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<sub>2</sub> feed levels; O<sub>2</sub>/EtOH ratios of 0.5 and 0.75, respectively.

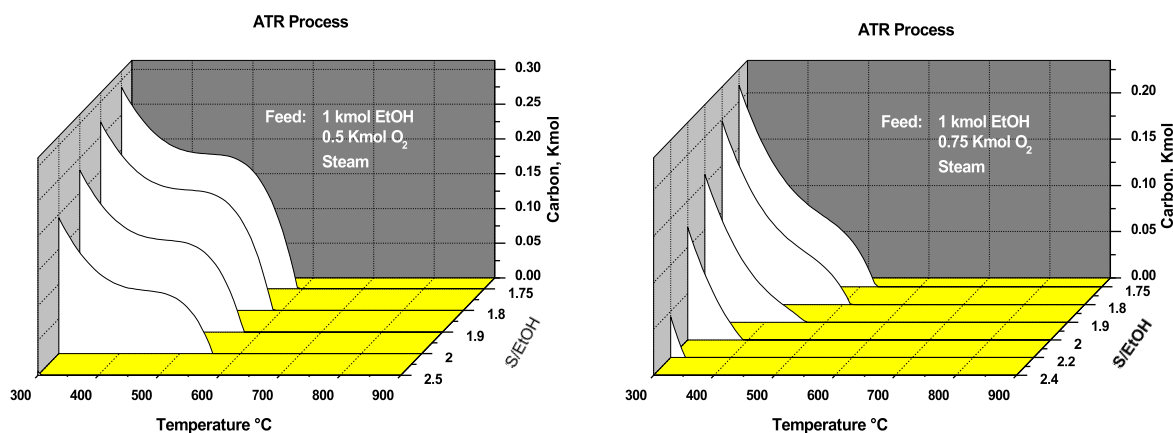


Figure 2. Carbon Formation for the ATR process at O<sub>2</sub>/EtOH ratios of 0.5 and 0.75 as a function of T and S/EtOH ratios

From this Figure it can be seen that at O<sub>2</sub>/EtOH = 0.5 carbon formation is predicted at a low temperature range of 300-600°C and S/EtOH < 2 within the ATR system as high as 0.28 kmol at 300°C. Greater temperatures from this region will prevent carbon to be formed in this reaction system. However, If the O<sub>2</sub> content is increased to a level of O<sub>2</sub>/EtOH = 0.75 this will be traduced in a reduction of the carbon formation region accompanied with lower temperatures at higher S/EtOH ratios. Maximum temperature for carbon formation was reduced to 524°C 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<sub>2</sub> content for the ATR process can be seen in Figure 3, where the O<sub>2</sub> content in the feed is increased to a level of O<sub>2</sub>/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 temperatures.



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

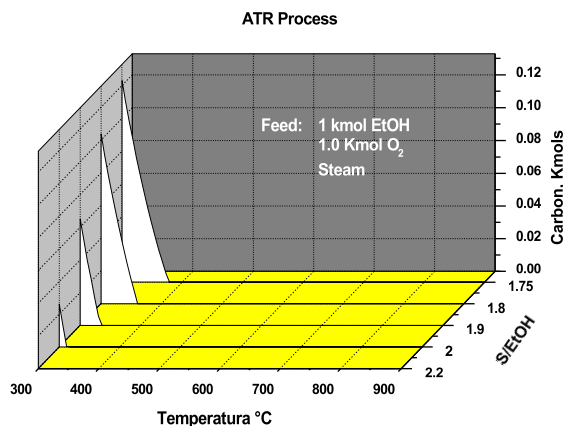
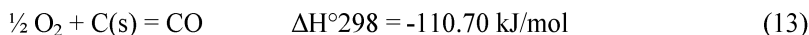
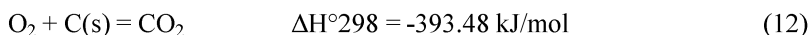


Figure 3. Carbon Formation for the ATR process at  $\text{O}_2/\text{EtOH} = 1.0$  as a function of  $T$  and  $S/\text{EtOH}$

The gasification equilibrium is also dependent on the steam to EtOH ratio and the temperature of the system. For instance, at  $S/\text{EtOH}$  ratios of 2 and greater, carbon is completely gasified at temperatures of  $400^\circ\text{C}$  and greater. This behavior can also be seen when the equilibrium content of carbon oxides are carefully examined. As the  $\text{O}_2$  content in the feed is increased the equilibrium content of the carbon oxides ( $\text{CO}$  and  $\text{CO}_2$ ) 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  $\text{CO}_2$  at an  $\text{O}_2/\text{EtOH} = 1.0$  and, when there is insufficient oxygen  $\text{O}_2/\text{EtOH} < 0.5$ , gasification to  $\text{CO}$  is thermodynamically favorable at temperatures above  $500^\circ\text{C}$ . Nevertheless, carbon formation apart from reaction (11) can also be generated through the following reactions:



Therefore, there is a complex network of reactions involved in the entire process. However the main fact is that  $\text{O}_2$  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  $S/\text{EtOH}$  and temperature for the AER-ATR reaction system at  $\text{O}_2/\text{EtOH}$  of 0.1 and 0.25, respectively. Feed to each system consisted in 1 kmol of ethanol, 2.5 kmol of  $\text{CaO}$  and the corresponding amount of steam for each  $S/\text{EtOH}$  ratio. For the case of  $\text{O}_2/\text{EtOH} = 0.1$  the  $S/\text{EtOH}$  ratio was varied from 0 to 1.85, while for  $\text{O}_2/\text{EtOH} = 0.25$  this changed from 0 to 1.6.

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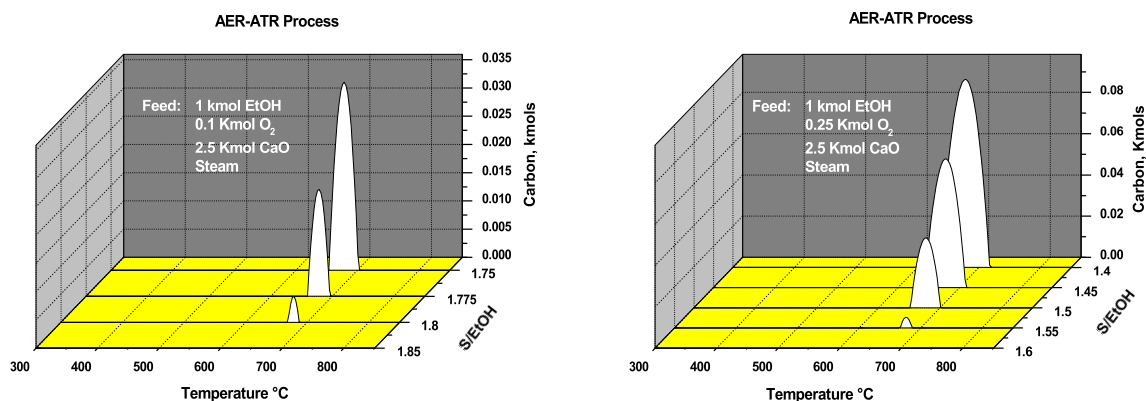


Figure 4. Carbon Formation for the AER-ATR process at  $O_2/EtOH = 0.1$  and  $0.25$  as a function of  $T$  and  $S/EtOH$ . Here it can be seen that the effect of combining the AER and the ATR reforming modes resulted in carbon free regions located at lower  $S/EtOH$  ratios. For example at  $O_2/EtOH = 0.1$  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 ( $650 - 800^\circ C$ ). 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  $1.2$ .

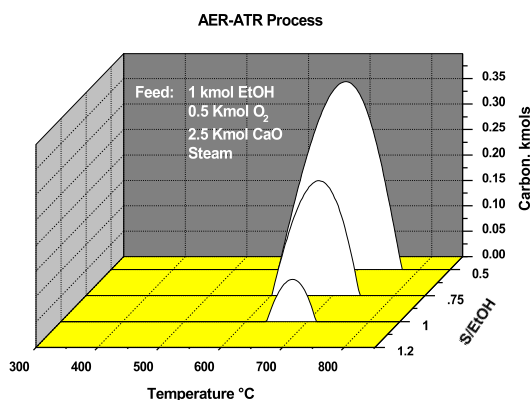


Figure 5. Carbon Formation for the AER-ATR process at  $O_2/EtOH = 0.5$  and  $0.25$  as a function of  $T$  and  $S/EtOH$ . Here the increase in  $O_2$  content within the absorption enhanced reforming of ethanol caused that the lower limit for carbon formation in terms of  $S/EtOH$  to be reduced. 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

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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 insure carbon free operation. 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 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 to 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 show 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. Equilibrium Thermodynamic Results for the Autothermal Conditions for the Reforming Processes Studied

FEED, kmols		S/EtOH	Adiabatic T ( $\Delta H = 0$ )	Product Composition % mol				H <sub>2</sub>
CaO	O <sub>2</sub>	Molar Ratio	(°C)	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	kmols
-	-	3	334	13.4	0.1	25.0	61.5	0.3
-	-	6.5	$\Delta H > 0$	71.7	8.1	19.4	2.8	4.7
-	0.1	3	312	18.0	0.1	27.0	54.9	0.4
-	0.1	6.5	403	27.3	0.6	26.4	45.7	2.7
-	0.25	3	475	42.5	2.5	26.7	28.3	1.5
-	0.25	6.5	390	36.7	0.4	28.6	34.2	1.2
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	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
2.5	-	3	481	90.8	0.0	0.0	9.2	4.3
2.5	-	6.5	372	98.3	~0	~0	1.7	5.6
2.5	0.1	3	572	97.8	0.5	0.3	7.4	4.4
2.5	0.1	6.5	457	98.6	0.0	0.0	1.3	5.5
2.5	0.25	3	639	90.7	3.4	1.7	4.2	4.5
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
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-

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. Table 1 presents autothermal conditions for the SR process at S/EtOH = 3 an autothermal temperature of 334°C is found accompanied with a very poor hydrogen

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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 °C 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<sub>2</sub>. In the same Table the ATR reforming mode was also explored in terms of the autothermal condition. Here, different O<sub>2</sub>/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 enlarges when the excess steam is fed to the reaction system. At O<sub>2</sub>/EtOH = 0.1 and S/EtOH = 3.0 results in an adiabatic temperature of 312°C, which produce very small hydrogen product and purity furthermore, this condition is not kinetically feasible for practical purposes. Therefore, an increase in the O<sub>2</sub> content was explored and this was reflected in a gradual increase in the adiabatic temperature as well as in the hydrogen content and purity. For example at O<sub>2</sub>/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<sub>2</sub> purities of 42 and 63% respectively. As the oxygen content was increased the concentrations of carbon oxides (CO and CO<sub>2</sub>) 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 performed by several authors in the literature [14, 19, 29, 30].

Also in Table 1 the AER process was evaluated in terms of the adiabatic conditions 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. 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 [31]. However these conditions are moderately endothermic with a  $\Delta H_R = + 196.5$  kJ/kmol. The values reported in Table 1 for the autothermal conditions 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<sub>2</sub>) 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 continue operation of this process.

On the other hand, Table 1 also presents results of the AER-ATR operating mode process proposed in the present work. Here, different O<sub>2</sub>/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<sub>2</sub>/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 % of carbon oxides (CO and CO<sub>2</sub>). 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<sub>2</sub>/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<sub>4</sub> selectivities were 16 and 14%, respectively, for a total selectivity to undesired minor products 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 is much lower and minor products are 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<sub>2</sub>/EtOH = 0.3 and using CaO as a CO<sub>2</sub> 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. A further increase in oxygen content to a value of O<sub>2</sub>/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%. This behavior can be explained in terms of an increase of the carbon oxides content (CO and CO<sub>2</sub>) that presumably promote the ethanol partial oxidation reactions thus producing gaseous carbon species that eventually is traduced in 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<sub>2</sub>/EtOH range of 0.3-0.4, S/EtOH = 6.5 and an adiabatic temperature range of 590-627°C.

#### 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<sub>2</sub> gas product. Results indicate no carbon formation at steam to ethanol ratios less than stoichiometric values (S/EtOH ≤ 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 insure 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 686°C combined with CaO as a solid CO<sub>2</sub> absorbent. The use of a CO<sub>2</sub> 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 ensure a carbon free operation at O<sub>2</sub> content in the feed in the order of O<sub>2</sub>/EtOH = 1.0 and temperatures lower than 400°C at all reaction temperatures. In the case of the AER-ATR process at oxygen contents of about O<sub>2</sub>/EtOH = 0.5, S/EtOH ratios greater than 1.2 are

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needed in order to insure 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 insure 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<sub>2</sub>/EtOH range of 0.3-0.4, S/EtOH = 6.5 and an adiabatic temperature range from 590-627°C.

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