Thermodynamic and Kinetics Modeling of H_2 Production by dry Reforming of Ethanol With CO_2 Evolution

R. B. Pallares Sámano, M. R. Baray Guerrero, J. Salinas Gutiérrez, V. Guzmán Velderrain, V. Collins Martínez, A. López Ortiz[*]

Departamento de Materiales Nanoestructurados, Centro de Investigación en Materiales Avanzados, S.C.,
Miguel de Cervantes 120, Chihuahua, Chih., México, 31109, México.
*Tel: 6144394815, Fax 6144394884, mail: alejandro.lopez@cimav.edu.mx

ABSTRACT

A viable alternative to fossil fuels is to make use of H_2 from renewable sources as an energy carrier or as a clean fuel. Steam reforming of hydrocarbons is the conventional process to produce H_2, with the drawbacks that presents low efficiency combined with high operational costs and CO_2 being emitted into the atmosphere. An alternative to this process is the dry reforming of hydrocarbons, which employs CO_2 to produce hydrogen-syngas and the use of ethanol as a renewable feedstock which would prevent CO_2 emission into the atmosphere. One innovative approach is the use of a solid carbonate to serve as a source of CO_2 for this process. Thus, exposing the solid carbonate to high temperatures (reaction temperature), this decomposes emitting CO_2, which is used as raw material along with ethanol (EtOH) to produce hydrogen-synthesis gas. The present work aims to perform a thermodynamic and kinetic simulation study to explore reaction conditions close to equilibrium for a high syngas-H_2 production, under the dry reforming of EtOH. $CaCO_3$ was used as source of CO_2 for the reaction system. The thermodynamic study was performed using the HSC software and the studied conditions were: T = 300-1000 °C, $CaCO_3$/EtOH molar ratio = 1-3. Results showed that at T ≥ 755 °C and $CaCO_3$/EtOH ≥ 2.2, a free carbon formation syngas is produced. Maximum H_2 production was obtained at 855 °C and $CaCO_3$/EtOH ≥ 2.2, while the highest concentration of H_2 was produced at 755 °C. Furthermore, a process and kinetics simulations were performed through ASPEN-Plus and CKS, respectively and based on experimental data taken from the literature for the dry reforming of EtOH. Results indicate that at 900 ºC and $CaCO_3$/EtOH = 2 ratio, the estimated value of H_2 purity was very similar to that obtained by the thermodynamic equilibrium analysis.

Keywords: CO_2 dry reforming, thermodynamic and kinetics modelling

1. Introduction

Today, one of the major technological challenges is the search for energy alternatives to fossil fuels and their impact on the environment. A viable option is to make use H_2 as an energy carrier or as a clean fuel from renewable sources such as biomass, solar energy, etc., and converted to electricity by fuel cells that provide high efficiency electricity with only steam as a clean gas exhaust. However, an efficient generation of hydrogen from the main energy carrier is a key condition for the commercialization of fuel cells [1–5].

Ethanol (EtOH) can be a considered a suitable feedstock to produce hydrogen through many catalytic processes. In comparison with other fuels, ethanol has several advantages. It can be produced through the fermentation of biomass or renewable raw materials, including energy plants, waste materials from agro-industries or forestry residue materials, organic municipal solid waste, etc. Ethanol produced from these raw materials are generally named biomass-derived ethanol or bioethanol. Hydrogen produced from bioethanol presents the significant advantage of being nearly CO_2 neutral, since the carbon dioxide released into the atmosphere during ethanol processing is re-absorbed in the growth of the biomass, and therefore, there is no net release of carbon dioxide into the atmosphere [6].

Ethanol can be converted into hydrogen through steam reforming [7–15], partial oxidation [16–21], autothermal reforming (oxidative reforming) [22–27] and dry reforming (CO_2 reforming, DRE) [28–31]. Although ethanol steam reforming, partial oxidation and autothermal reforming have been extensively studied, dry reforming of ethanol has received much less attention. Furthermore, CO_2 is a greenhouse gas and as a consequence ethanol reforming with CO_2 is an interesting approach for the conversion of CO_2 into syngas or hydrogen, which can further be converted into high value chemicals such as methanol, synthetic fuels, urea, etc.

One innovative approach for the syngas/hydrogen production through the dry reforming of ethanol process (DRE) is the use of a solid carbonate (such as $CaCO_3$) to serve as a source for CO_2 in this process. Thus, exposing the solid carbonate to the high temperatures of the DRE reaction (such as 900 °C), decomposes the solid carbonate through:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad\qquad \Delta H^0{}_{298} = 178 \text{ kJ/mol} \qquad\qquad (1)$$

thus, emitting CO_2, which is then used as raw material along with ethanol (EtOH) to produce hydrogen-synthesis gas by:

$$C_2H_6O + CO_2 = 3CO + 3H_2 \qquad\qquad \Delta H^0{}_{298} = 296.70 \text{ kJ/mol} \qquad\qquad (2)$$

Then, by combining the CO_2-releasing decomposition of $CaCO_3$ with the CO_2-consuming reforming of C_2H_6O, it is possible to simultaneously coproduce CaO and syngas in a single reaction, represented by:

$$C_2H_6O + CaCO_3 = CaO + 3CO(g) + 3H_2(g) \qquad\qquad \Delta H^0{}_{298} = 649.78 \text{ kJ/mol} \qquad\qquad (3)$$
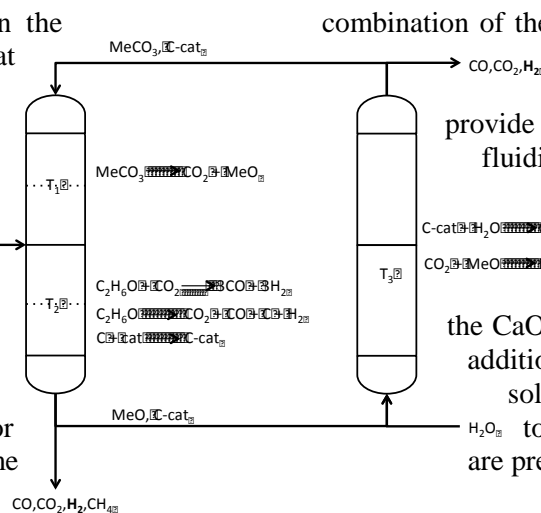
Important advantages that this reaction scheme offers over steam reforming are (a) the formation of a suitable H_2/CO ratio for use in Fischer-Tropsch synthesis and (b) more desirable thermodynamic properties, for example large heat of reaction and reversibility for chemical energy transmission systems such as chemical looping [32].

Moreover, although the dry reforming concept has environmental benefits and economic advantages, there are only a few commercial processes based on the CO_2 reforming reaction such as the CALCOR and SPARG processes [33, 34]. This can be due to the fact that a major limitation of this process arises from the formation of carbon deposits, which can cause a significant deactivation of the reforming catalyst.

One promising approach for the dry reforming concept is the so called "Catforming" process, which consists of two circulating fluidized beds. A downer for the endothermic CO_2 reforming and a riser for the catalyst regeneration. In the process scheme, the transport of the solids between both reactors allows for a period of catalyst regeneration involving coke combustion [35]. Even though the fact that the reforming reactor is to be operated under unfavorable carbon formation conditions, coke will inevitably be deposited on the active sites of the catalyst.

Our proposal is based in the combination of these two new approaches to the dry reforming process that syngas and/or hydrogen in use of a solid carbonate will reforming of ethanol in a inevitable carbon deposits characterize this removed by steam in a separate (riser), and at the same time along with the production of regenerated catalyst and the back to the reforming reactor Details of this process scheme can be used to produce an efficient manner. First, the provide the necessary CO_2 for the dry fluidized bed and secondly, the on the catalyst that process will be gasification with fluidized bed reactor the CaO will carbonate back to $CaCO_3$ additional syngas. Finally, the sold carbonate will be recycled to complete a full reaction cycle. are presented in Figure 1 below.

Figure process scheme:

MeCO$_3$, C-cat   CO,CO$_2$,**H$_2$**

$MeCO_3 \longrightarrow CO_2 + MeO$

C$_2$H$_6$O

... T$_1$ ...   ... T$_2$ ...

$C_2H_6O + CO_2 \longrightarrow 3CO + 3H_2$
$C_2H_6O \longrightarrow CO_2 + CO + C + H_2$
$C + cat \longrightarrow C\text{-}cat$

MeO, C-cat

CO,CO$_2$,**H$_2$**,CH$_4$

$C\text{-}cat + H_2O \longrightarrow CO + CO_2 + cat + H_2$
$CO_2 + MeO \longrightarrow MeCO_3$

T$_3$

H$_2$O

Figure 1. H_2 production by dry reforming of ethanol with CO_2 evolution and catalyst regeneration

In this process MeO (CaO) can be any metal oxide capable to be carbonated at the required conditions of the process. $MeCO_3$ ($CaCO_3$) is any carbonated metal oxide and cat is any dry reforming catalyst. It is important to point out that heat integration plays an essential role for the feasibility of this process. In the dry reforming reactor at least two highly endothermic reactions take place (1 and 2), while at the gasification reactor the carbon oxidation and MeO carbonation are highy exothermic reactions. Therefore, it is expected that presumably, some of the necessary heat for the reforming reactor will be provided by the gasification reactor and their solid carried products (MeO and cat).

Therefore, the present work aims to perform thermodynamic, process and kinetic simulation studies to explore reaction conditions close to equilibrium for a high syngas-H_2 production, under the dry reforming of EtOH, using $CaCO_3$ as a source of CO_2 for the dry reforming reaction system.

2. Simulation Methods

2.1. Thermodynamic Method

Thermodynamic calculations employed the 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 nonstoichiometric method). Details of this technique can be found elsewhere [36]. All calculations were performed using the equilibrium module of the HSC chemistry software for windows [37]. 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 at a fixed mass balance, constant pressure and temperature. At the ethanol dry reforming system the gaseous species included were: ethanol, ethylene, ethane, acetone, acetaldehyde, acetic acid, C_2H_6O, CO, CH_4, CO_2, H_2, and H_2O, while solid species were: C, CaO and $CaCO_3$.

During the thermodynamic simulation work the reaction temperature was varied in the range of 300-1000 °C at 1 atm. While, carbonate to ethanol molar ($CaCO_3$/EtOH) was varied from 1-5. It is important to notice that all the present simulation calculations are based on theoretical thermodynamic considerations and these are to be taken as a guide to further experimental evaluation of the reaction systems, since no heat and mass diffusional limitations as well as kinetics effects were taken into account for the conformation of the present thermodynamic analysis.

2.2. Process Simulation Method

Process simulation calculations were performed using of Aspen-plus$^{©}$ Engineering Process Simulator. This is a program for simulation of chemical processes in which the analysis of chemical processes as well as heat integration can be made.

Therefore, this simulator was employed for the analysis of the process scheme of Figure 1. The modules of Aspen-Plus that were used to evaluate the reaction system were: the RGibbs (Gibbs Reactor) and RStoic (Stoichiometric Reactor) units, wherein RGibbs method is based on the Gibbs free energy minimization technique for multiphase reactions and material balance, while RStoic is based on known fractional reaction conversions. Cyclone were used to separate solid and gas streams, mixers were also used to combine several gas and/or solid streams, while heat exchangers allowed heat balance and integration.

2.3. Kinetics Simulation Method

Kinetics simulations were performed through the CKS software [38] and based on experimental data taken from the literature. The CKS program conveniently simulates chemical reactions. Its stochastic simulation technique is fast and accurate, and is very suitable for a wide variety of reactions. Specifically the software is based in a stochastic process, which is used to characterize a sequence of random variables (stochastic) that evolve according to another variable, usually time. Each of the random variables of the process has its own probability distribution function and, between them, can be correlated. CKS require the specification of the chemical reaction mechanism in a conventional notation, the rate constants for each step, and the reactions conditions (temperature and pressure). The same program calculates concentration versus time curves as well as the pressure, volume and temperature data. Simulations with CKS are not limited to homogeneous systems; a wide variety of non-homogeneous reactions, for example, between gases and solids or in a fluidized reactors, can be successfully simulated by using this simple technique.

In this the present kinetic simulation a reaction mechanism for the dry reforming of ethanol combined with the CO_2 evolution from $CaCO_3$ was proposed and compared with experimental data for the ethanol steam reforming system, which kinetically behaves similarly to the dry reforming system. Kinetic data results (CKS) from simulation were then compared to the equilibrium data previously obtained in the thermodynamic section of the present study.

3. Results and discussion

3.1. Thermodynamic Analysis

The production of hydrogen and other compounds (CO, CO_2 and C) at a temperature range of 300-1000 °C and $CaCO_3/C_2H_6O$ molar ratios from 1 to 3 were analyzed on the basis of thermodynamic analysis. At the studied conditions the conversion of ethanol was always greater than 99.99% and it can be considered for practical purposes that the conversion is complete. Figure 1 shows the equilibrium content (dry basis) in kmol/mol of EtOH fed as a function of temperature and $CaCO_3/EtOH$ molar ratio for H_2, CO, CO_2 and C species.

In this Figure it is evident that H_2 and CO mols at equilibrium increase monotonically with increasing temperature from 300 to 1000 °C and this can be explained in terms of the equation (1), which reflects the temperature dependence of the equilibrium constant as described by Wang et al. [39]. In contrast, CO_2 content at equilibrium is dominated by the combination of reactions (1) and (2), which at temperatures from 300-700°C shows an average of 0.45 kmols of CO_2, thus reflecting the excess of CO_2 being fed according to the stoichiometric $CaCO_3/EtOH$ ratio of 1 needed according to reaction (3). However, higher temperatures will produce a greater CO_2 content especially at $CaCO_3/EtOH$ molar ratios greater than 2. This can be explained in terms of reaction 2, in which high temperatures (greater than 600 °C) will increase the CO_2 evolution.

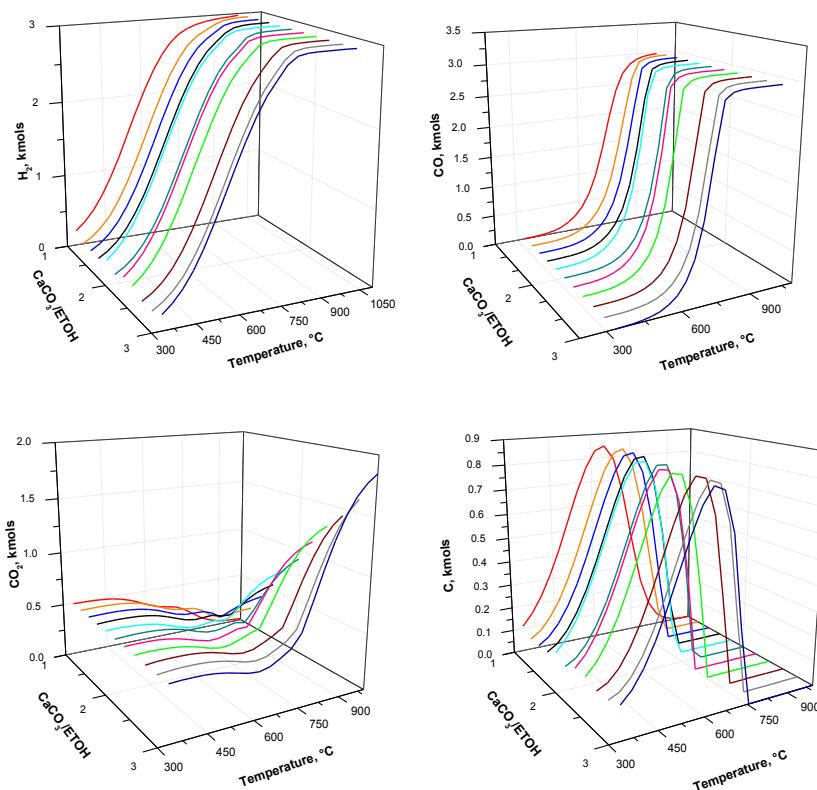Figure 2. Equilibrium content for the DRE process with CO_2 evolution

This is why the CO_2 content increases to values greater than 1 at temperatures closer to 900 °C and $CaCO_3$/EtOH ratios ≥ 2. Furthermore, CO_2 content at ratios lower than ≈ 1.5 are smaller than the average 0.45 kmols. This is explained by the fact that CO_2 is almost completely consumed by the DRE reaction (2), since the stoichiometric amount of CO_2 needed according to reaction (3) is of 1 mol of $CaCO_3$ per mol of EtOH fed to the reaction system. Also in this Figure the carbon content is plotted as a function of temperature and $CaCO_3$/EtOH ratio. Here, it is evident that lower temperatures than 750 °C will produce carbon with a maximum generated at temperatures around 650 °C. This was expected, since previous thermodynamic analysis using gaseous CO_2 as a feed also confirmed this behavior [39]. Therefore, temperatures greater than around 750 °C and $CaCO_3$/EtOH ratios ≥ 2.2 will insure a carbon free operation region for the DRE combined with CO_2 evolution by a solid carbonate. This behavior can be explained ion terms of the Boudouard reaction:

$$2CO \rightarrow CO_2 + C \qquad\qquad \Delta H^0_{298} = \text{-175.81 kJ/mol} \qquad\qquad (4)$$

That is why at temperatures greater than 750 °C the CO content significantly increases, since the above reaction is no longer thermodynamically favoured and consequently no carbon formation is possible.

A more careful analysis of the generated data allows to conclude that according to the previous thermodynamic analysis data optimum conditions in order to produce a maximum hydrogen production and carbon free operation is at temperatures greater than 755 ° C and at $CaCO_3$/EtOH ratios ≥ 2.2.

3.2. Process Simulation

Figure 3 presents a diagram of the process simulation scheme employed during the simulation of the DRE with CO_2 evolution and catalyst regeneration. The catalyst was not included in this simulation due to the fact that this has to be determined based on future experimental research.
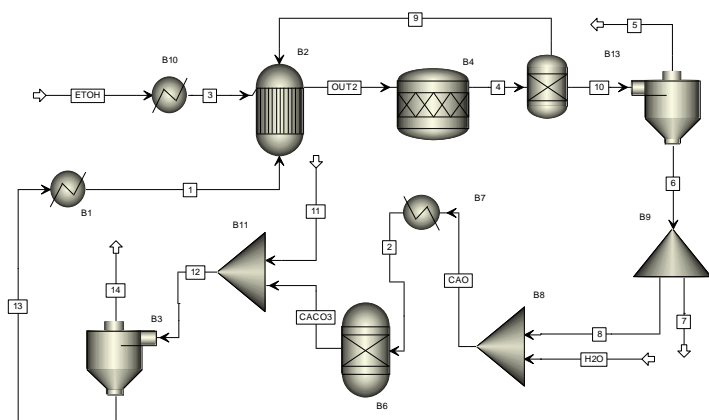

Figure 3. Process simulation diagram for the DRE with CO_2 evolution and catalyst regeneration

This process starts with the EtOH feed of 1 kmol/h to being preheated to 900°C and fed to the DRE reactor, along with a mixture of 1 and 0.83 kmol/h of $CaCO_3$ and CaO, respectively. The reactor duty was 508,034.6 kJ/h at 900 °C and 1 atm. The reactor products were fed to a stoichiometric reactor where carbon was allowed to be formed by reaction (4) using an experimental reaction conversion of 0.6 based on the data from Hu et al. [40] at present DRE reaction conditions. It is important to state that even though at 900 °C and feed $CaCO_3$/EtOH ratio used here, thermodynamically no carbon is formed, experimentally this happens. Therefore, a more realistic result can be obtained by considering the combination of equilibrium results and the corresponding experimental carbon formation. The CO_2 formed by the Boudouard reaction (1.798 kmol/h) were recycled to the DRE reactor (B2). After this reactor a H_2/CO molar ratio of 0.998 was obtained with only negligible amounts of CH_4 and H_2O. Additionally, 0.77 kmol/h of carbon were formed. Then a cyclone was used to separate the gases from the solids and the gas product stream 5 included: 2.223 kmol/h of H_2 and 2.226 kmol/h of CO, while 1.83 kmol/h of CaO were sent to the regenerator along with the carbon. Stream 6 solids were divided at separator B9 and stream 7 was discarded for circulation and balance purposes, while stream 8 containing 1.28 kmol/h of CaO and 0.54 kmol/h of C were combined with 1.2 kmol/h of steam in mixer B8, preheated to 770 °C and then fed to the regenerator reactor, where the carbon gasification and CaO carbonation reactions took place. The product from the regenerator consisted in 0.45 kmol/h of $CaCO_3$ along with 0.83 kmol/h of CaO and 0.913 kmol/h of H_2.Then in mixer B11 0.74 kmol/h of $CaCO_3$ were added to this last stream followed by separation of the gaseous products at cyclone B3, where a mixture of mainly H_2 and steam exited at stream 14. The remaining solids composed by 1 kmol/h of $CaCO_3$ and 0.83 kmol/h of CaO were preheated to 900 °C (B1) to be recycled back to the DRE reactor B2.

Table 1 below summarizes results from the process simulation of selected streams. In this Table it can be seen that the gaseous output stream of the process are streams 5 and 14. Stream 5 presents a H_2/CO ratio of about 1, while stream 14 is almost a pure H_2 stream. This is very convenient, since these two streams can be combined to obtain a specific desired H_2/CO ratio as in the case of the Fischer-Tropsch process for the production of a specific fuel mixture composition.

Comparing the process simulation results with one of the actual commercial dry reforming process called Calcor, the H_2/CO ratio obtained with this process is 0.42 from a natural gas feed [33]. Modifications to this process include a membrane reactor to improve the syngas yield and separation of the CO_2 produced along with the syngas by a standard amine technology and to recycle this stream back to the dry reformer. Furthermore, as stated earlier, the mayor problem of this technology is the carbon formation over the reforming catalyst causing deactivation and constant catalyst replacement or regeneration. Another commercial process is the Sparg that produce a H_2/CO ratio of 1.8 and suppressing the carbon formation by using a partially sulfur poisoned nickel catalyst [34]. However, product synthesis gas from this process still contains about 2.7% of methane.

Moreover, in the case of the present simulation a solution to this problem is offered. Furthermore, it is important to notice that the present process simulation effort in only a first attempt to show the possible advantages of the proposed technology, while production costs and a more deep energy analysis is further needed in order to assess the feasibility the present proposed technology.

3.3. Kinetics Simulation

In order to perform the kinetic simulation of the ethanol dry reforming combined with CO_2 evolution it is required to establish the corresponding reaction mechanism. This was selected according to the following criteria: because there are scarce references of studies related to the kinetics of dry reforming of ethanol and because Jankhah [41] has experimentally found that the kinetic behavior of both the dry and the steam reforming of ethanol follow a very similar kinetic mechanism it was decided that in the present kinetic simulation a reaction mechanism for the dry reforming of ethanol combined with the CO_2 evolution be simulated with kinetic experimental data reported for the steam reforming of ethanol reaction system.
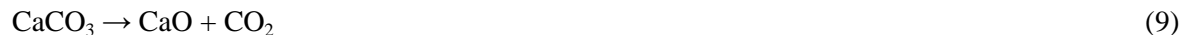
Table 1. Summary of process simulation results of selected streams

Stream Name Mole Flow kmol/hr	ETOH	1	OUT2	4	5	7	CAO	CACO$_3$	11	14
CACO$_3$	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.45	0.55	0.00
CO$_2$	0.00	0.00	1.02	1.80	0.00	0.00	0.00	0.02	0.00	0.02
CAO	0.00	0.83	1.83	1.83	0.00	0.55	1.28	0.83	0.00	0.00
C$_2$H$_6$O	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	0.00	0.00	3.77	2.23	2.23	0.00	0.00	0.04	0.00	0.04
H$_2$	0.00	0.00	2.22	2.22	2.22	0.00	0.00	0.91	0.00	0.91
C	0.00	0.00	0.00	0.77	0.00	0.23	0.54	0.00	0.00	0.00
CH$_4$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.03
H$_2$O	0.00	0.00	0.78	0.78	0.78	0.00	1.20	0.22	0.00	0.22
Total Flow kmol/hr	1.00	1.83	7.80	7.02	5.23	0.78	3.02	2.51	0.55	1.23
Total Flow kg/hr	46.07	146.84	169.27	159.98	80.83	33.63	21.62	8.30	55.05	8.30
Total Flow l/min	1262.85	0.86	12515.39	11272.81	8386.75	0.18	1778.18	1547.73	0.34	1547.73
Temperature °C	650.00	900.00	900.00	900.00	900.00	900.00	810.46	650.00	650.00	650.00

For this endeavor it was needed to find the experimental data that followed the same reaction mechanism as in the steam reforming system. In the present case it was found that the Eley-Rideal mechanism fulfilled this purpose. Becerra et al. [42] found that an Eley-Rideal type model described adequately the main reaction of the CO_2 reforming of methane, while Akande [43] reported experimental data and found that the steam reforming of ethanol over a Ni/Al_2O_3 catalysts followed also the Eley-Rideal type model resembling the CO_2 reforming of methane mechanism found by Becerra et al. This mechanism is based on the interaction between gas-phase molecules which react directly with adsorbed species; in the present reaction system, not all the reactants were adsorbed on the catalyst surface. Accordingly, the surface reaction involve adsorbed and non-adsorbed substances, so that it is considered a subset of Langmuir mechanisms in which one of the reactants is not absorbed in the catalyst [44].

Because the dry reforming of EtOH and CO_2 evolution is a complex system of reactions and following the above criteria, the combination of the reaction steps of two catalytic mechanisms was proposed; on one side the catalytic dry reforming of methane and on the other the catalytic steam reforming of ethanol, thereby obtaining a catalytic reaction mechanism equivalent to the kinetic process to be simulated. This mechanism is described by the reaction steps given below:

$$C_2H_6O + S \rightarrow C_2H_6O\text{-}S \tag{5}$$

$$C_2H_6O\text{-}S + S \rightarrow CH_4O\text{-}S + CH_2\text{-}S \tag{6}$$
$$CH_4O\text{-}S \rightarrow CH_2\text{-}S + H_2O \tag{7}$$
$$CO + H_2O \rightarrow CO_2 + H_2 \tag{8}$$
$$CaCO_3 \rightarrow CaO + CO_2 \tag{9}$$
$$2CH2\text{-}S + 2CO_2 \rightarrow 4CO + 2H_2 + 2S \tag{10}$$
$$C_2H_6O + CaCO_3 \rightarrow CaO + 3CO + 3H_2 \tag{11}$$

where steps from reactions (5) to (10) represent the proposed mechanism, and the overall reaction is represented by reaction (11), here S represents an active site for the adsorption of species, while $C_2H_6O\text{-}S$ represents an adsorbed transient specie. This mechanism was inserted into the CKS program with initial concentrations of C_2H_6O, $CaCO_3$ and S of 1, 2 and 3 mol/L, respectively. Kinetic parameters (e.g. A_o, E_a, etc.) for the above reactions were taken from experimental data on the steam reforming of ethanol reported by Patel et al. [45]. Figure 4 presents results for the kinetic simulation of the dry reforming of ethanol combined with CO_2 evolution at temperature of 900 °C and based on the proposed reaction mechanism.
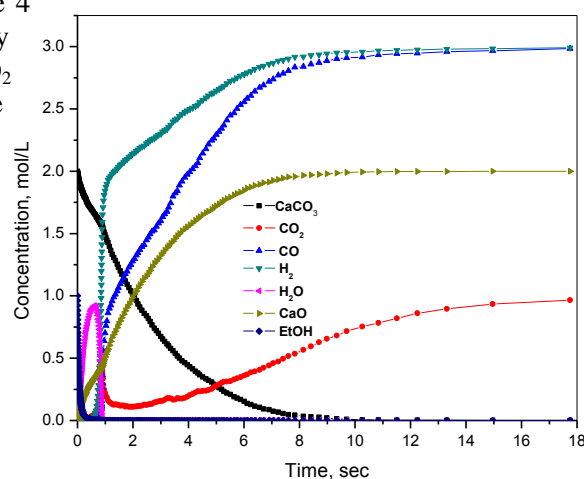

Figure 4. Kinetic simulation re of the diagram for the DRE with CO_2 evolution

Concentration profiles from Figure 4 reflect the nature of the proposed mechanism. Ethanol is fully converted almost instantly, while water is produced from the surface reaction equation (7) to later be consumed at about 1 second by the eater gas shift reaction (8). Hydrogen is formed almost instantly as a consequence of the WGS reaction and then at a slower rate at about 1.5 sec when the CO_2 is being formed by the decomposition of the $CaCO_3$ reaction (9), while CO is initially hindered by the WGS to later be enhanced by surface reaction (10). CO_2 evolution can be clearly observed in Figure 4, since this starts gradually and at about 9 sec the complete conversion of reaction (9) is achieved. This was also reflected in the H_2 and the CO concentrations reaching both 3 mol/L. All these results agree well with the previous

thermodynamic analysis and process simulation results in the sense that at carbon free conditions (900°C and $CaCO_3$/EtOH = 2.2) the H_2/CO molar ratio was almost 1, with also 3 mols H_2 and CO being formed.

4. Summary and perspectives

The present work a thermodynamic, process and kinetic simulation studies were performed to explore reaction conditions close to equilibrium for a high syngas-H2 production, under the dry reforming of EtOH. $CaCO_3$ was used as source of CO_2 for the reaction system, instead of high purity CO_2 employed in the current dry reforming technology. Results showed the feasibility that at $T \geq 755$ °C and $CaCO_3$/EtOH ≥ 2.2, a free carbon formation syngas can be produced. Maximum H_2 production can be obtained at 855 °C and $CaCO_3$/EtOH ≥ 3, while the highest concentration of H_2 was produced at 755 °C. Furthermore, a process and kinetics simulations performed through ASPEN-Plus and CKS, respectively and based on experimental data taken from the literature for the dry reforming of EtOH indicate that at 900 ºC and $CaCO_3$/ETOH = 2 ratio, the estimated value of H_2 purity was very similar to that obtained by the thermodynamic equilibrium analysis. Finally, these results can be taken as a basis for future experimental and theoretical studies in search for a suitable catalyst and conditions to evaluate the present proposed technology.

References

[1] Armor JN. The multiple roles for catalysis in the production of hydrogen. Appl Catal A 1999; 176(2): 159–76.

[2] Joensen F, Rostrup-Nielsen JR. Conversion of hydrocarbons and alcohols for fuel cell. J Power Sources 2002; 105(2):195–201.

[3] Peña MA, Gomez JP, Fierro JLG. New catalytic routes for syngas and hydrogen production. Appl Catal A 1996; 144:7–57.

[4] Goltsov VA, Veziroglu TN, Goltsova LF. Hydrogen civilization of the future a new conception of the IAHE. Int J Hydrogen Energy 2006; 31:153–9.

[6] Velu S, Satoh N, Gopinath CS, Suzuki K. Oxidative reforming of bio-ethanol over CuNiZnAl mixed oxide catalysts for hydrogen production. Catal Lett 2002; 82(1–2):145–52.

[7] Garcia EY, Laborde MA. Hydrogen production by the steam reforming of ethanol: thermodynamic analysis. Int J Hydrogen Energy 1991; 16:307–12.

[8] Vasudeva K, Mitra N, Umasankar P, Dhingra SC. Steam reforming of ethanol for hydrogen production: thermodynamic analysis. Int J Hydrogen Energy 1996; 21:13–8.

[9] Haga F, Nakajima T, Miya H, Mishima S. Catalytic properties of supported cobalt catalysts for steam reforming of ethanol. Catal Lett 1997; 48:223–7.

[10] Mariño FJ, Cerrella EG, Duhalde S, Jobbagy M, Laborde MA. Hydrogen from steam reforming of ethanol. Characterization and performance of copper–nickel supported catalysts. Int J Hydrogen Energy 1998; 23:1095–101.

[11] Liguras DK, Kondarides DI, Verykios XE. Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts. Appl Catal B 2003; 43(4): 345–54.

[12] Aboudheir A, Akande A, Idem R, Dalai A. Experimental studies and comprehensive reactor modeling of hydrogen production by the catalytic reforming of crude ethanol in a packed bed tubular reactor over a Ni/Al_2O_3 catalyst. Int J Hydrogen Energy 2006; 31:752–61.

[13] Cavallaro S, Mondello N, Freni S. Hydrogen produced from ethanol for internal reforming molten carbonate fuel cell. J Power Sources 2001; 102(1):198–204.

[14] Rostrup-Nielsen J, Trimm DL. Mechanisms of carbon formation on nickel-containing catalysts. J Catal 1977; 48: 155–65.

[15] Trimm DL. Coke formation and minimization during steam reforming reactions. Catal Today 1997; 37(3):233–8.

[16] Fierro V, Klouz V, Akdim O, Mirodatos C. Oxidative reforming of biomass derived ethanol for hydrogen production in fuel cell applications. Catal Today 2002; 75(1–4):141–4.

[17] Liguaras DK, Goundani K, Verykios XE. Production of hydrogen for fuel cells by catalytic partial oxidation of ethanol over structured Ru catalysts. Int J Hydrogen Energy 2004; 29:419–27.

[18] Ioannides T. Thermodynamic analysis of ethanol processors for fuel cell applications. J Power Sources 2001; 92:17–25.

[19] Cheekatamarla PK, Finnerty CM. Synthesis gas production via catalytic partial oxidation reforming of liquid fuels. Int J Hydrogen Energy 2008; 33:5012–9.

[20] Hsu SN, Bi JL, Wang WF, Yeh CT, Wang CB. Low-temperature partial oxidation of ethanol over supported platinum catalysts for hydrogen production. Int J Hydrogen Energy 2008; 33:693–9.

[21] Wang WJ, Wang YQ. Thermodynamic analysis of partial oxidation of biomass-derived ethanol for hydrogen-rich gas generation. Int J Hydrogen Energy 2008; 33:5035–44.

[22] Deluga GA, Salge JA, Schmidt LD, Verykios XE. Renewable hydrogen from ethanol by autothermal reforming. Science 2004; 303:993–7.

[23] Cavallaro S, Chiodo V, Vita A, Freni S. Hydrogen production by auto-thermal reforming of ethanol on Rh/Al_2O_3 catalyst. J Power Sources 2003; 123:10–6.

[24] Huang L, Xie J, Chen R, Chu D, Chu W, Hsu AT. Effect of iron on durability of nickel-based catalysts in auto-thermal reforming of ethanol for hydrogen production. Int J Hydrogen Energy 2008; 33:7448–56.

[25] Youn MH, Seo JG, Cho KM, Park S, Park DR, Jung JC, et al. Hydrogen production by auto-thermal reforming of ethanol over nickel catalysts supported on Ce-modified mesoporous zirconia: effect of Ce/Zr molar ratio. Int J Hydrogen Energy 2008; 33:5052–9.

[26] Srisiriwat N, Therdthianwong S, Therdthianwong A. Oxidative steam reforming of ethanol over Ni/Al_2O_3 catalysts promoted by CeO_2, ZrO_2 and CeO_2–ZrO_2. Int J Hydrogen Energy 2009; 34:2224–34.

[27] Youn MH, Seo JG, Park S, Jung JC, Park DR, Song IK. Hydrogen production by auto-thermal reforming of ethanol over Ni catalysts supported on ZrO_2: effect of preparation method of ZrO_2 support. Int J Hydrogen Energy 2008; 33:7457–63.

[28] De Oliveira-Vigier K, Abatzoglou N, Gitzhofer F. Dryreforming of ethanol in the presence of a 316 stainless steel catalyst. Can J Chem Eng 2005; 83:978–84.

[29] Tsiakaras P, Demin A. Thermodynamic analysis of a solid oxide fuel cell system fuelled by ethanol. J Power Sources 2001; 102(1):210–7.

[30] Jankhah S, Abatzoglou N, Gitzhofer F. Thermal and catalytic dry reforming and cracking of ethanol for hydrogen and carbon nano filaments' production. Int J Hydrogen Energy 2008; 33:4769–79.

[31] Ruckenstein E, Wang HY. Carbon deposition and catalytic deactivation during CO_2 reforming of of CH_4 over Co/g-Al_2O_3 catalysts. J Catal 2002; 205(2):289–93.

[32] Halmann M., Seinfeld A., Thermoneutral Coproduction of Calcium Oxide and Syngas by Combined Decomposition of Calcium Carbonate and Partial Oxidation/CO_2-Reforming of Methane, Energy & Fuels 2003, 17, 774-778.

[33] Teuner, St. C.; Neumann, P.; Von Linde, F. The Calcor Standard and Calcor Economy Processes. Oil Gas Eur. Mag. 2001, 3, 44.

[34] Udengaard, N. R.; Bak Hansen, J. H.; Hanson, D. C.; Stal, J. A. Sulfur promoted Reforming Process lowers Syngas Hydrogen/Carbon Monoxide Ratio. Oil Gas J. 1992, 90 (10), 62.

[35] Solh E., T.; Jarosch, K.; de Lasa, H. Catalytic Dry Reforming of Methane in a CREC Riser Simulator Kinetic Modeling and Model Discrimination. Ind. Eng. Chem. Res. 2003, 42, 2507.

[36] Collins-Martínez V. Escobedo Bretado M., Meléndez Zaragoza M., Salinas Gutiérrez J., López Ortiz A. Absorption enhanced reforming of light alcohols (methanol and ethanol) for the production of hydrogen: Thermodynamic modeling, Int J Hydrogen Energy 2013; 38:12539–553.

[37] Roine A. Chemical reaction and equilibrium software with extensive thermo-chemical database. Outokumpu HSC 6.0 Chemistry for windows; 2010.

[38] IBM Almaden Research Center. 1995. Introduction: Getting Started. IBM Corporation. Chemical Kinetics Simulator 1.0 User´s Manual.v-vii.

[39] Wang W., Wang Y., Dry reforming of ethanol for hydrogen production: Thermodynamic investigation, Int J Hydrogen Energy 2009; 34:5382–5389.

[40] Hu X., Lu G., Syngas production by CO_2 reforming of ethanol over Ni/Al_2O_3 catalyst, Catal Comm 10 (2009) 1633–1637.

[41] [X] Jankhah, Sepideh, Ethanol reforming with carbon dioxide, Memory of Masters in applied science with a major in chemical engineering, Université de Sherbrooke, 2007, available at:
http://savoirs.usherbrooke.ca/bitstream/handle/11143/1386/MR37883.pdf?sequence=1&isAllowed=y

[42] Becerra M. A., Iriarte M. E., and Castro-Luna A. E., Catalytic Activity of A Nickel on Alumina Catalyst in The CO_2 Reforming of Methane, React.Kinet.Catal.Lett Vol. 79, No. 1, 119-125, 2003.

[43] Akande A. J., Production of Hydrogen by Reforming of Crude Ethanol, Master of Science Thesis, Department of Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, February 2005.

[44] Izquierdo Torres, J. F. Cinética de las reacciones químicas. Barcelona: Universitat Barcelona (2004).

[45] Patel M., Jindal T. K., and Pant K. K., Kinetic Study of Steam Reforming of Ethanol on Ni-Based Ceria−Zirconia Catalyst, Ind. Eng. Chem. Res. 2013, 52, 15763−15771