

PRODUCTION OF HYDROGEN FROM THE STEAM AND OXIDATIVE REFORMING OF LPG: THERMODYNAMIC AND EXPERIMENTAL STUDY

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(Submitted: April 12, 2014 ; Revised: November 22, 2014 ; Accepted: November 22, 2014)

Abstract - The objective of this paper was to use a thermodynamic analysis to find operational conditions that favor the production of hydrogen from steam and oxidative reforming of liquefied petroleum gas (LPG). We also analyzed the performance of a catalyst precursor, LaNiO₃, in order to compare the performance of the obtained catalyst with the thermodynamic equilibrium predictions. The results showed that it is possible to produce high concentrations of hydrogen from LPG reforming. The gradual increase of temperature and the use of high water concentrations decrease the production of coke and increase the formation of H₂. The reaction of oxidative reforming of LPG was more suitable for the production of hydrogen and lower coke formation. Furthermore the use of an excess of water (H₂O/LPG =7.0) and intermediate temperatures (973 K) are the most suitable conditions for the process.

Keywords: Hydrogen; Liquefied petroleum gas; Reform; Thermodynamic analysis.

INTRODUCTION

The great interest in the use of fuel cells in homes, transportation, and chemical industries has stimulated the demand for large-scale production of hydrogen (Ahmed and Krumpelt, 2001; Cheekatamarla and Finnertya, 2006; Rossi *et al.*, 2009; Montané *et al.*, 2011; Dantas *et al.*, 2012). In addition, the application of more stringent environmental laws in relation to gaseous pollutants such as ash, hydrocarbons (HCs), nitrogen oxides (NOx) and carbon monoxide

(CO) in industrial processes has required the development of cleaner technologies (Barreto *et al.*, 2003).

However, for fuel cell systems to be employed on a large scale, it is necessary to develop processes to produce high-purity hydrogen and to store that hydrogen at the same place where it will be used. Therefore, obtaining hydrogen from compounds that already have a distribution network, such as natural gas, oil, ethanol (in the case of Brazil) and liquefied petroleum gas (LPG), is a requirement to fully implement a hydrogen-based economy (Ayabe *et al.*,

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This is an extended version of the manuscript presented at the
VII Brazilian Congress of Applied Thermodynamics - CBTermo 2013, Uberlândia, Brazil.

2003; Gokaliler *et al.*, 2008; Jeong and Kang, 2010; Li *et al.*, 2010). Industrially, the most common route for hydrogen production has been steam reforming of methane (Rossi *et al.*, 2009), although there are several studies in the literature reporting the use of other compounds such as ethanol, propane and butane to obtain hydrogen (Montané *et al.*, 2011; Gokaliler *et al.*, 2008; Jeong and Kang, 2010; Li *et al.*, 2010).

The oxidative reforming, which involves coupling reactions of steam reforming and partial oxidation, seems to be a good route for hydrogen production, since it usually lowers catalyst deactivation due to coke deposition and improves the thermal balance, depending on the concentration of oxygen fed (Dias and Assaf, 2004). Recently, several studies have analyzed the use of propane (Silberova *et al.*, 2005; Faria *et al.*, 2008; Corbo and Migliardini, 2007), butane (Avci *et al.*, 2004; Ferradon *et al.*, 2010) and liquefied petroleum gas (LPG), a mixture in which the main components are propane and butane (Laosiripojana and Assabumrungrat, 2006; Moon, 2008), for hydrogen production.

The literature reports the use of transition metals such as Ni, Ru, and Rh for LPG reform reactions (Laosiripojana and Assabumrungrat, 2006; Moon, 2008; Laosiripojana *et al.*, 2011). For hydrocarbon reform reactions, nickel is usually a good choice since it presents good activity and stability. In addition, the cost of nickel is low when compared to noble metals, such as Pt and Rh. Usually, a good catalyst for reforming reactions should have a good metal dispersion. An alternative way to provide this property is the use of the perovskite structure as a catalyst precursor (ABO_3 , A = alkali metal, alkaline earth or rare earth, B = transition metal). These oxides have a structure that is able of accept a wide range of defects caused by partial substitution at the A and/ or B positions, which may provide interesting properties for the resulting catalysts (Lima *et al.*, 2010).

Although there are several literature reports that analyze the thermodynamics of the reforming of hydrocarbons to produce hydrogen (Diaz Alvarado and Garcia, 2010; Zeng *et al.*, 2010; Wang *et al.*, 2010), there are none that evaluated the effect of using LPG as the hydrocarbon source. There are some experimental studies available on LPG reform, which show the use of different types of catalysts, operating conditions and selectivities for H_2 and CO. (Laosiripojana and Assabumrungrat, 2006; Gokaliler *et al.*, 2008; Moon, D. J., 2008; Laosiripojana *et al.*, 2010; Laosiripojana *et al.*, 2011). However, the effects of operational parameters such as reaction tem-

perature, steam/carbon and oxygen/carbon ratios still are not clear in the literature. Therefore, thermodynamic analysis can be applied to this process in order to help to determine optimal conditions and operating parameters that can lead to the best experimental conditions, maximizing H_2 yield and minimizing coke formation, while reducing operational costs.

In this context, the objective of this paper was to use a thermodynamic analysis to find operational conditions that favor the production of hydrogen from steam and oxidative reforming of LPG. The variables studied were temperature and feed composition. We decided to fix the pressure at 1 atm for this study, since the literature reports that the best H_2 yields are obtained at this condition (Wang *et al.*, 2010; Wang *et al.*, 2011). In this work we also analyzed the performance of a catalyst precursor, $LaNiO_3$ (perovskite), in order to compare the performance of the obtained catalyst with the thermodynamic equilibrium predictions in the steam and oxidative reforming of LPG.

METHODOLOGY

Thermodynamic Analysis

In this work, Brinkley's stoichiometric method was used to minimize the Gibbs free energy (Walas, 1985). To apply this method, it is necessary to select a set of independent reactions representative of the reaction system, as well as the thermodynamic properties of all species considered. For each reaction considered, it is necessary to evaluate the equilibrium constant at the temperature considered at the reference pressure (usually taken as atmospheric pressure). For a system with i species and j reactions occurring, we have:

$$n_i = n_i^0 + \sum_j \nu_{ij} \varepsilon_j \quad (1)$$

n_i^0 is the number of moles of species i present in the feed and ε_j is the coordinate number of the reaction j .

The total derivative of the Gibbs free energy is given by:

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i \quad (2)$$

The equilibrium condition is achieved when the Gibbs free energy for the system reaches a minimum

value. At equilibrium, with T and P constant, we have:

$$d(nG) = \sum_i v_i \mu_i d\varepsilon \quad (3)$$

In equilibrium conditions, $d(nG) = 0$ for $\forall d\varepsilon \neq 0$

$$\sum_i v_i \mu_i = 0 \text{ and } \mu_i = G_i^o + RT \ln \left(\frac{\hat{f}_i}{f_i^o} \right) \quad (4)$$

Replacing the chemical potential (μ_i) in the equilibrium condition, we have for each reaction j :

$$\sum_i v_i \left[G_i^o + RT \ln \left(\frac{\hat{f}_i}{f_i^o} \right) \right] = 0 \quad (5)$$

This leads to

$$\Delta G_j^o + RT \sum_i \ln \left(\frac{\hat{f}_i}{f_i^o} \right)^{v_i} = 0 \quad (6)$$

The species i activity (\hat{a}_i) is, by definition:

$$\hat{a}_i = \frac{\hat{f}_i}{f_i^o} \quad (7)$$

in which f_i^o is the fugacity of species i at the system temperature and pressure of 1 atm and \hat{f}_i is the fugacity of species i in the mixture. Replacing the activity (\hat{a}_i) in Equation (7), we have:

$$\Delta G_j^o + RT \sum_i \ln \hat{a}_i^{v_i} = 0 \quad (8)$$

Rearranging, we have:

$$\exp \left[-\frac{\Delta G_j^o}{RT} \right] = \prod \hat{a}_i^{v_{ij}} \quad (9)$$

Therefore, for each reaction j , the equilibrium constant of each reaction is calculated by:

$$K_j = \prod \hat{a}_i^{v_{ij}} = \exp \left[\frac{-\Delta G_j^o}{RT} \right] \quad (10)$$

v_{ij} is the stoichiometric coefficient of the species i in the reaction j .

In the gas phase, the activity can be evaluated by:

$$\hat{a}_i = \hat{f}_i = y_i \hat{\phi}_i P \quad (11)$$

where y_i is the mole fraction, $\hat{\phi}_i$ is the fugacity coefficient and P is the reference pressure of 1 atm. We considered $f_i^o = 1$ atm because the values of formation energy were evaluated at 1 atm and, in this condition, the species can be considered to be an ideal gas. The operational conditions of the reaction system considered are atmospheric pressure and high temperature. In these conditions, the mixture in the gas phase can be considered to be an ideal gas mixture. This occurs because the intermolecular interaction parameter decreases with increasing temperature. For ideal gases, $\hat{\phi}_i = 1$, then $\hat{f}_i = y_i P$. Therefore

$$\hat{a}_i = y_i P \text{ and } K_j = \prod (y_i P)^{v_{ij}} \quad (12)$$

The activity of solid carbon can be considered equal to unity ($\hat{a}_c = 1$) because the fugacity of a solid is not very sensitive to pressure. We also considered that in the solid phase, there is just carbon (no gas is adsorbed on the solid). Therefore, $\hat{f}_c = f_c^o$.

The mole fraction of species i is given by:

$$y_i = \frac{n_i}{\sum_j n_j} \quad (13)$$

Since the equilibrium constant of each reaction is evaluated from Equation (10), it is necessary to calculate the change in the Gibbs free energy for the reaction j at a temperature T and pressure of reference of 1 atm. This calculation is done using Equations (14) to (17):

$$\frac{\Delta G_j}{RT} = \frac{\Delta G_j^o - \Delta H_j^o}{RT_0} + \frac{\Delta H_j^o}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_p_j}{R} dT - \int_{T_0}^T \frac{\Delta C_p_j}{RT} dT \quad (14)$$

$$\Delta G_j^o = \sum_i v_{ij} G_{fi}^o \quad (15)$$

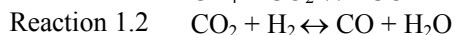
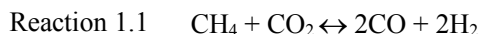
$$\Delta H_j^0 = \sum_i v_{ij} H_{fi}^0 \quad (16)$$

$$\Delta C p_j = \sum_i v_{ij} C p_i^o \quad (17)$$

The standard values of enthalpy and entropy, as well as heat capacity values, were obtained from the literature (Smith *et al.*, 2007).

Validation of the Computer Code

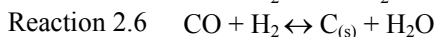
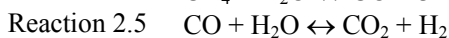
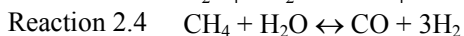
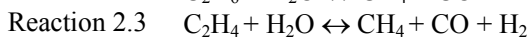
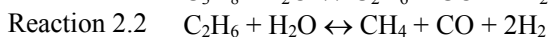
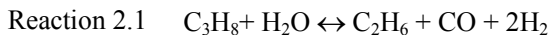
Data from the literature (Zeng *et al.*, 2010; Li *et al.*, 2008) were used to validate our computer program, which was based on Brinkley's method. The dry reform of methane was evaluated in three different operational conditions, as reported by Li and coworkers (2008). In the dry reform of methane, without feeding O₂, the relevant species include CH₄, H₂O, CO, CO₂, H₂ and solid carbon. In this case, just 3 independent reactions are necessary to represent the system. The following reactions were used in this validation, which was called Case 1:



The conditions evaluated were:

- T = 973 K; P = 1 atm; O₂/CH₄ = 0; CO₂/CH₄ = 1
- T = 1073 K; P = 1 atm; O₂/CH₄ = 0; CO₂/CH₄ = 1
- T = 1073 K; P = 2 atm; O₂/CH₄ = 0; CO₂/CH₄ = 1

We also used another literature study to continue the validation of the computer program. Zeng and coworkers (2010) estimated the thermodynamic equilibrium composition for the oxidative steam reforming of propane. We used the data from this study relative to propane steam reform, without the presence O₂, in which the following species were considered: C₃H₈, C₃H₆, C₂H₆, C₂H₄, CH₄, CO, CO₂, H₂ and H₂O. In this case, the set of independent reactions chosen is presented below (Case 2):

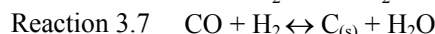
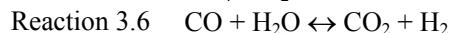
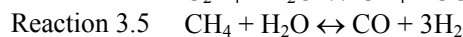
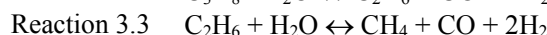
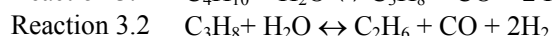
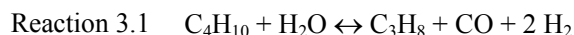


The followings conditions were tested, in this case:

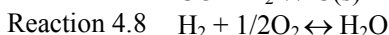
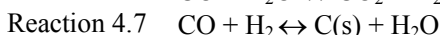
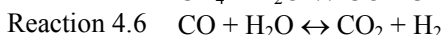
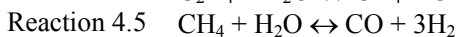
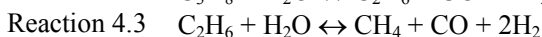
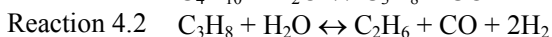
- T = 773 K; P = 1 atm; O₂/C₃H₈ = 0; H₂O/C₃H₈ = 5;
- T = 973 K; P = 1 atm; O₂/C₃H₈ = 0; H₂O/C₃H₈ = 3;
- T = 1173 K; P = 1 atm; O₂/C₃H₈ = 0; H₂O/C₃H₈ = 3.

LPG System

Recent experimental studies have shown that the LPG reforming reaction system can be represented by the following species: C₄H₁₀, C₃H₈, C₂H₆, C₂H₄, CH₄, CO, CO₂, H₂, H₂O and solid carbon (Laosiripojana and Assabumrungrat, 2006; Moon, 2008). In this work, two distinct cases were studied. The first one, called "Case 3", involved butane, propane and steam in several proportions. This system was represented by the seven linearly independent reactions listed below.



For the second analysis (Case 4) one more species (oxygen) was added to represent the oxidative system. This system was described by the seven reactions already listed above plus reaction 4.8.



The following equations were used to evaluate the mole fractions of H₂, CO, CH₄, CO₂ on a dry basis and conversion of butane and propane formed at equilibrium in Case 3.

$$y_i = \frac{n_i}{\left(\sum_{j=1}^N n_j \right)} \quad (18)$$

$$\%C_4H_{10} = \frac{\left((n_{C_4H_{10}})_{in} - (n_{C_4H_{10}})_{out} \right) * 100}{(n_{C_4H_{10}})_{in}} \quad (19)$$

$$\%C_3H_8 = \frac{\left((n_{C_3H_8})_{in} - (n_{C_3H_8})_{out} \right) * 100}{(n_{C_3H_8})_{in}} \quad (20)$$

In Equation (18), n_i and n_j are the mole numbers of species i and j in the reactor outlet stream (H_2 , CH_4 , CO , CO_2 , C_2H_4 , C_2H_6 , C_3H_8 , C_4H_{10}), respectively. For Case 4 that represents the reaction of oxidative reforming of LPG, the equations were the same as those used in Case 3, but with the number of moles of unreacted oxygen added to the denominator of Equations (18), (19) and (20).

For the solution of the reaction system, we used Maple12® with a few restrictions on the search range. The restrictions are relative to the number of atoms of carbon, hydrogen and oxygen present in the system. The reaction coordinate numbers (ϵ_j) are not independent. The two restrictions that we used were related to the extent of reactions 3.4 and 3.6 for Case 3 and reactions 4.4 and 4.6 for Case 4.

The energy demand (Q) was defined as the amount of energy necessary to heat the LPG and water from 298 K up to the desired temperature in the reactor (Equation (20)). Both LPG and water were considered to be pure components in the feed. For LPG, the energy demand is just that necessary to heat this gas from 298 K to the desired temperature (Equation (21)). In the case of H_2O , at the reference temperature (298 K), this species is a liquid and at the reactor temperature it is a vapor (referred to in this study as steam). Therefore, the energy demand for water (Equation (21)) is composed of three terms: (i) the first one related to the energy necessary to heat the liquid water from 298 K to 373 K at 1 atm of pressure; (ii) the second term represents the vaporization heat at 373 K and 1 atm; (iii) the last term represents the heating of vaporized water (steam) from 373 K to the reactor temperature at 1 atm.

$$Q = \Delta H_{LPG} + \left(\frac{S}{C} \right) \Delta H_S \quad (21)$$

$$\Delta H_{LPG} = \int_{T_0}^T C_{pLPG} dT \quad (22)$$

$$\Delta H_S = \int_{T_0}^{T_n} C_{pS}^L dT + \Delta H_S^{vap} \Big|_{T_n} + \int_{T_n}^T C_{pS}^g dT \quad (23)$$

where $[Q] = \text{kJ}/(\text{mol of LPG in the feed})$, $\frac{S}{C} = \text{Steam/LPG ratio in the feed}$, $C_{pS}^L = \text{Heat capacity of}$

liquid water, $T_n = \text{Normal boiling temperature}$; $\Delta H_S^{vap} \Big|_{T_n} = \text{Molar latent heat of vaporization at } T_n$; $C_{pS}^g = \text{Heat capacity of water in the gas phase}$.

Experimental

Catalyst Preparation

The perovskite precursor ($LaNiO_3$) was prepared by a precipitation method adapted from Lima and coworkers (2010). An aqueous solution of sodium carbonate (0.5 M) was rapidly added to a freshly prepared aqueous solution of $La(NO_3)_3 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ under vigorous stirring, until reaching pH 8. Then, the formed precipitate was washed and filtered under vacuum to remove remaining contaminant ions. The obtained solid was dried in a furnace at 338 K for 20 h and calcined under a flow of synthetic air ($50 \text{ mL} \cdot \text{min}^{-1}$) in two stages: first at 723 K (heating rate of $1.5 \text{ K} \cdot \text{min}^{-1}$) for 4 hours and finally at 1173 K (heating rate of $5 \text{ K} \cdot \text{min}^{-1}$) for 6 hours.

Catalytic Test

(a) Steam Reforming of LPG

Steam reforming of LPG was carried out in a fixed-bed tubular quartz reactor operated isothermally at atmospheric pressure. The ‘‘U’’ shaped reactor was $\frac{1}{4}$ in. (outside diameter) with a small bulb where the catalyst was placed. This reactor was positioned in the experimental unit inside a high temperature furnace equipped with a thermocouples and a temperature controller. The multipurpose experimental unit was composed of a set of 4 mass flow controllers that were responsible to feed the desired gases at each step of the experiment. In addition, there was a high pressure pump to feed liquid water. This water was evaporated in a section maintained at 453 K and the obtained gas then mixed with the other reactants coming from the mass flow controllers. All the lines were heated at 453 K to ensure that there was no condensation of the water coming from the pump. Prior to the tests, the perovskite-type oxides ($\sim 10 \text{ mg}$) diluted with quartz (40 mg) were reduced using pure H_2 ($30 \text{ mL} \cdot \text{min}^{-1}$) and a linear temperature increase ($10 \text{ K} \cdot \text{min}^{-1}$) up to 973 K. This temperature was kept for 2 h. After this, the sample was purged under Ar flow ($30 \text{ mL} \cdot \text{min}^{-1}$) at the same reduction temperature for 30min. The steam reforming of LPG was carried out at 873, 973, 1073, and 1173 K using feeds with $H_2O / (C_4H_{10} - C_3H_8)$ ratios equal to 3.5, 7.0 and 10.0. The total flow rate was

kept at $200 \text{ mL}\cdot\text{min}^{-1}$, containing $20 \text{ mL}\cdot\text{min}^{-1}$ of hydrocarbons. The reactor effluent was analyzed using a gas chromatograph.

With the objective of ensuring the kinetic regime, tests varying the residence time (W/F) were performed. The reaction of the steam reforming of LPG was tested using different masses of a similar catalyst precursor ($\text{La}_{0.95}\text{Ce}_{0.05}\text{NiO}_3$) (5, 10, 20, 40 mg) and total flow at $200 \text{ mL}\cdot\text{min}^{-1}$ and $300 \text{ mL}\cdot\text{min}^{-1}$. Figure 1 shows C_4H_{10} and C_3H_8 conversions. It can be seen that the region of kinetic control ends at approximately W/F equal to $0.1 \text{ mg}\cdot\text{min}\cdot\text{L}^{-1}$. Thus, for all the tests in this work, a W/F ratio of $0.05 \text{ mg}\cdot\text{min}\cdot\text{L}^{-1}$ with a total flow rate of $200 \text{ mL}\cdot\text{min}^{-1}$ and mass equals to 10 mg of catalyst were used for catalytic tests.

(b) Oxidative Reforming of LPG

The same system and conditions were used for the oxidative reforming of LPG. The tests were carried out at 873, 973, 1073, and 1173 K using a feed with a

$(\text{H}_2\text{O}/(\text{C}_4\text{H}_{10}-\text{C}_3\text{H}_8))/\text{O}_2$ ratio equal to 7.0/1.0/0.25 with a total flow rate of $200 \text{ mL}\cdot\text{min}^{-1}$.

RESULTS AND DISCUSSION

Validation of Thermodynamic Data

Table 1 shows the validation of the computational code used in this work comparing the data obtained here and those estimated by Li and coworkers (2008) considering the system of dry reforming of methane (Case 1). At all analyzed conditions, the errors, in general, were very small for all variables (conversions of CH_4 and CO_2 , as well as H_2 and C(s) yield). Table 2 presents the comparison of predicted thermodynamic equilibrium data obtained by Zeng and coworkers (2010) and the ones calculated in this study for propane reforming (Case 2). Again, very similar values of H_2 , CO , H_2O and CH_4 yields were observed, indicating a good reliability of the results obtained in this present study.

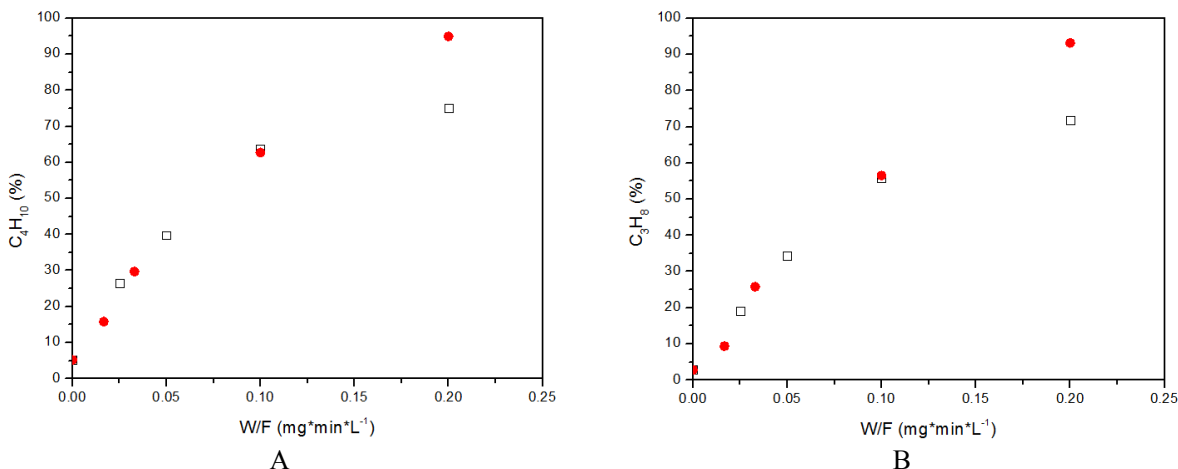


Figure 1: Conversion of butane and propane tests of steam reforming of LPG at 873 K to define the region where there is only kinetic effect. \square $200 \text{ mL}\cdot\text{min}^{-1}$; \bullet $300 \text{ mL}\cdot\text{min}^{-1}$.

Table 1: Validation of computational code using data obtained by Li and coworkers (2008) for CO_2 reforming of methane.

Conditions	Results	Li <i>et al.</i> ,(2008)	This paper
T=973 K P=1atm $\text{O}_2/\text{CH}_4=0$ $\text{CO}_2/\text{CH}_4=1$	Conversion of CH_4 Conversion of CO_2 H_2 yield C yield	90.9 % 66% 75% 0.60 moles	90.8% 66.58% 75.84% 0.5421 moles
T=1073 K P=1atm $\text{O}_2/\text{CH}_4=0$ $\text{CO}_2/\text{CH}_4=1$	Conversion of CH_4 Conversion of CO_2 H_2 yield C yield	96% 89% 90% 0.18 moles	95.9% 89.18% 91% 0.1731 moles
T=1073 K P=2atm $\text{O}_2/\text{CH}_4=0$ $\text{CO}_2/\text{CH}_4=1$	Conversion of CH_4 Conversion of CO_2 H_2 yield C yield	Not reported Not reported Not reported 0.29 moles	92.7% 82.6% 83.7% 0.28 moles

Table 2: Validation of computational code using data obtained by Zeng and coworkers (2010) for propane steam reform.

Conditions	Results	Zeng <i>et al.</i> ,(2010)	This paper
T=773 K P=1atm O ₂ /C ₃ H ₈ =0 H ₂ O/C ₃ H ₈ =5	CH ₄ yield (mol/mol C ₃ H ₈) CO yield (mol/mol C ₃ H ₈) H ₂ yield (mol/mol C ₃ H ₈) C yield (mol/mol C ₃ H ₈)	~1.7 ~0.2 ~2.7 ~0.0	1.7720 0.1820 2.6308 0.0443
T=973 K P=1atm O ₂ /C ₃ H ₈ =0 H ₂ O/C ₃ H ₈ =3	CH ₄ yield (mol/mol C ₃ H ₈) CO yield (mol/mol C ₃ H ₈) H ₂ yield (mol/mol C ₃ H ₈) C yield (mol/mol C ₃ H ₈)	~0.45 ~1.67 ~5.3 ~0.5	0.4512 1.6657 5.4326 0.5485
T=1173 K P=1atm O ₂ /C ₃ H ₈ =0 H ₂ O/C ₃ H ₈ =3	CH ₄ yield (mol/mol C ₃ H ₈) CO yield (mol/mol C ₃ H ₈) H ₂ yield (mol/mol C ₃ H ₈) C yield (mol/mol C ₃ H ₈)	~0.09 ~2.9 ~6.5 ~0.0	0.0917 2.8814 6.7462 0.0027

Comparison Between Thermodynamic and Experimental Data for Steam Reforming of LPG

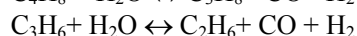
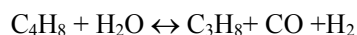
Table 3 presents the equilibrium constants for the reactions considered in the steam reforming system calculated at different temperatures (873 to 1173 K). We can observe that reactions 3.1, 3.2, 3.3, 3.4, 3.5 are endothermic, while reactions 3.6 and 3.7 are exothermic. Therefore, as usually is demonstrated in both experimental and theoretical studies, the use of higher temperatures favors both hydrogen production (reactions 3.1 to 3.5) and reduction of coke deposition (reaction 3.7). However, the use of high temperatures increases the operational costs and, therefore it is important to evaluate the effect of variables such as temperature and steam to hydrocarbon ratio on the hydrogen production, coke deposition and energy demand.

Table 3: Equilibrium constants for the reactions considered in the LPG steam reform as a function of temperature.

	873 K	973 K	1073 K	1173 K
K1	2.398 x 10 ³	2.358 x 10 ⁴	1.517 x 10 ⁵	7.097 x 10 ⁵
K2	2.236 x 10 ³	2.198 x 10 ⁴	1.412 x 10 ⁵	6.596 x 10 ⁵
K3	1.060 x 10 ⁴	9.081 x 10 ⁴	5.225 x 10 ⁵	2.230 x 10 ⁶
K4	3.466 x 10 ⁵	3.899 x 10 ⁵	4.287 x 10 ⁵	4.630 x 10 ⁵
K5	5.092 x 10 ⁻¹	1.218 x 10 ¹	1.636 x 10 ²	1.424 x 10 ³
K6	2.710 x 10 ⁰	1.641 x 10 ⁰	1.104 x 10 ⁰	8.018 x 10 ⁻¹
K7	4.313 x 10 ⁰	6.284 x 10 ⁻¹	1.308 x 10 ⁻¹	3.550 x 10 ⁻²

Usually LPG is represented by a mixture of the following species: C₄H₁₀, C₄H₈, C₃H₈ and C₃H₆ (Laosiripojana and Assabumrungrat, 2006; Moon, 2008). In order to better understand the influence of the presence of saturated and unsaturated compounds in the feed on the final equilibrium compositions of hydrogen, LPGs with different amounts of saturated and unsaturated hydrocarbons were evaluated. For this

analysis, two additional reactions were added to case 3, representing the reaction of butene and propene with water to form CO, H₂ and a smaller chain hydrocarbon.



The amount of water added was maintained at the stoichiometric value. The ratios of butane/ propane/ butene/propene studied were: A-0.5:0.5:0.0:0.0, B-0.35:0.35:0.17:0.13, C-0.17:0.13:0.35:0.35 and D-0.0:0.0:0.5:0.5. The composition A contains just saturated hydrocarbons and D just unsaturated ones. C represents LPG composed of 70% of saturated and D 30% of unsaturated hydrocarbons. The number of moles of hydrogen is shown in Table 4. Although it can be noted that the feeds containing higher amounts of saturated hydrocarbons led to higher H₂ yields, it is clear that the effect of temperature is more pronounced than the effect of feed composition. Therefore, in order to simplify the analysis and the experimental set up, we decided to consider LPG only as a mixture of saturated hydrocarbons (50% C₄H₁₀-50% C₃H₈).

Table 4: Effect of the presence of unsaturated hydrocarbons on the number of moles of hydrogen obtained at equilibrium. Molar ratios of propane: butane: propene: butane evaluated: A - 0.5:0.5:0.0:0.0, B - 0.35:0.35:0.17:0.13, C - 0.17:0.13:0.35:0.35, D - 0.0: 0.0:0.5:0.5.

T (K)	Moles of H ₂			
	A	B	C	D
873.15	4.3990	4.2332	3.9827	3.7741
973.15	6.9371	6.6905	6.3168	6.0018
1073.15	7.7096	7.4517	7.0564	6.7227
1173.15	7.9147	7.6562	7.2570	6.9191

The calculated equilibrium conversions of C_4H_{10} and C_3H_8 , mole fractions of H_2 , CO , CO_2 , CH_4 and H_2/CO ratio are shown in Figure 2 ($H_2O/LPG = 3.5/0.5C_4H_{10}-0.5C_3H_8$). It can be noted that, at all temperatures, the equilibrium conversion for C_3 and C_4 species is total. Major differences can be observed when analyzing the influence of temperature on the mole fractions of methane, carbon dioxide, carbon monoxide and hydrogen. The temperature increase causes a decrease in the mole fraction of methane and an increase of the mole fractions of CO and H_2 . This fact can be related to the steam reforming of methane (reaction 3.5) which, as shown in Table 3, has an endothermic character. The increase in temperature also causes a decrease in the mole fraction of carbon dioxide. Probably, the reverse water gas shift reaction is favored, which explains the drop in the CO_2 mole fraction, with simultaneous increase of CO mole fraction as the temperature raised.

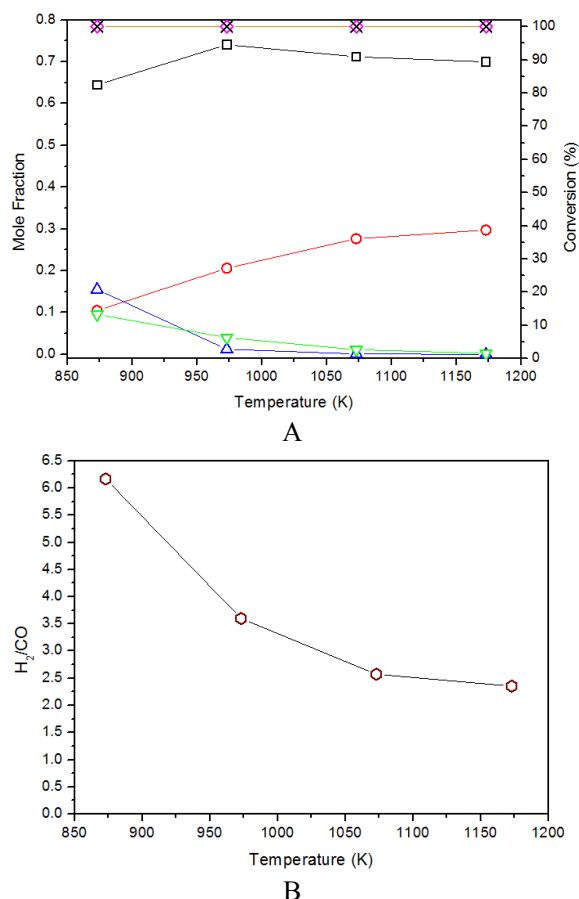
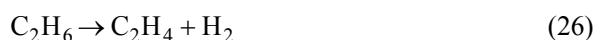
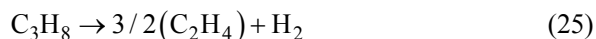
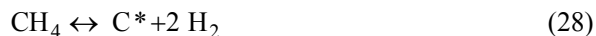


Figure 2: Calculated C_4H_{10} and C_3H_8 conversions, mole fractions and H_2/CO ratio at equilibrium as a function of temperature ($3.5H_2O/0.5C_4H_{10}-0.5C_3H_8$). □ Y_{H_2} ; ○ Y_{CO} ; △ CH_4 ; ▽ Y_{CO_2} ; ◇ C_4H_{10} Conversion; × C_3H_8 Conversion.

Laosiripojana and Assabumrungrat (2006) studied experimentally the steam reforming of LPG at 973 – 1173 K. According to these authors, the use of high temperatures favors the decomposition of butane and propane according to the following equations:

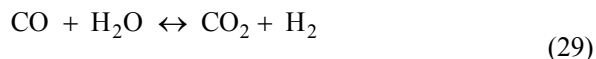


At high temperatures, in this system, the final state is the production of C^* and H_2 , because this condition favors the decomposition of methane.



Thus, a simplified mechanism for the LPG reform could be described as: the hydrocarbons are broken into solid carbon (C^*) and hydrogen on the catalyst surface, which is desorbed as H_2 . Then, the solid carbon is oxidized to form CO or CO_2 by oxygen provided by water molecules. The balance between these two processes can be verified by the H_2/CO ratio. The stoichiometric value of the H_2/CO ratio for LPG reforming is equal to 2.29. When the H_2/CO ratio is higher than this value, probably the first process of the mechanism occurs and, since CO is not forming, carbon accumulates on the catalyst surface.

The data in Figure 2B show that at 873 K the H_2/CO ratio is 6.3, indicating that at lower temperatures the first stage of the reform mechanism of butane and propane – conversion of the hydrocarbons into H_2 and C^* – is occurring. Consequently, due to the use of milder temperatures, the oxygen from water does not remove all the carbon deposits, resulting in a low CO yield. However, above 1125 K, the H_2/CO ratio is approximately equal to that predicted by stoichiometry, suggesting that the use of high temperatures is necessary to prevent carbon accumulation. This result is in agreement with Zhu and coworkers (2010), who also obtained lower values of the H_2/CO ratio at higher temperatures during the steam reforming of methane. For CO_2 , the temperature rise generates a decrease in the fraction of this compound. In accordance with Avci and coworkers (2004), the water-gas-shift reaction is slightly exothermic, indicating that at higher temperatures the formation of CO_2 is impaired.



$$\Delta H = -41.2 \text{ kJ/mol}$$

Figure 3 shows the experimental results obtained for the reaction of steam reforming of LPG under the same conditions assessed by thermodynamics ($H_2O/LPG = 3.5/0.5C_4H_{10}-0.5C_3H_8$ and $T = 873 - 1173$ K). The catalyst precursor used in these tests was $LaNiO_3$ since it presented good results for reactions of hydrocarbon reforming (Lima *et al.*, 2010). In Figure 3A, it can be seen that the increase in temperature leads to higher propane and butane conversions, as expected (Avci *et al.*, 2004; Corbo and Migliardini, 2007). Most of the experimental data obtained in this study follow the same trends of the ones predicted by the thermodynamic analysis. H_2 mole fraction increases sharply from 873 K, stabilizing around 1073 K (0.67). CO mole fraction increases with increasing temperature; however, the amounts of CO_2 and CH_4 gradually decrease. According to Rostrup-Nielsen and Sehested (2002), for nickel-based catalysts, hydrocarbon molecules adsorb on the metal and suffer successive scissions. The resulting C^* species can react with oxygen species generated by the dissociation of water, or remain adsorbed on the active sites, resulting in deactivation of the catalyst. The H_2/CO ratio obtained experimentally (Figure 3B) confirms that, below 973 K, the formation of C^* and H_2 occurs, but probably due to the low temperature the second process, which is the production of CO or CO_2 , is inhibited.

In the search for the best operational conditions, we evaluated the amount of water necessary to ob-

tain 1% or less of carbon deposition under equilibrium conditions for the steam reform of LPG. The feed was again a mixture of 0.5 mol of C_4H_{10} and 0.5 mol of C_3H_8 with different amounts of water. The results are presented in Figure 4. The number of moles of hydrogen obtained per mol of hydrocarbon fed (Figure 4A) increases sharply with the rise of both temperature and water in the feed. Figure 4B presents the number of moles of solid carbon obtained under the same conditions. It can be noted that the amount of solid carbon at equilibrium decreases with the increase of temperature and water fed. However, both variables probably will increase the operational costs.

Figure 5 shows the effect of excess water on the ratio H_2/CO experimentally obtained in the reaction of steam reforming of LPG as a function of temperature. Note that at high temperatures (above 1000 K), independent of the H_2O/LPG ratio used, the H_2/CO ratio decreases to values close to the stoichiometric one ($H_2/CO = 2.29$). However, the use of a large excess of water ($H_2O/LPG = 10$) did not lead to higher H_2 yields. Therefore, this condition is not recommended since it would have much higher energy costs. According to Wang and coworkers (2010), above 1000 K, regardless of the amount of water added in a hydrocarbon reform system, the H_2/CO ratio obtained is small and close to the stoichiometric value.

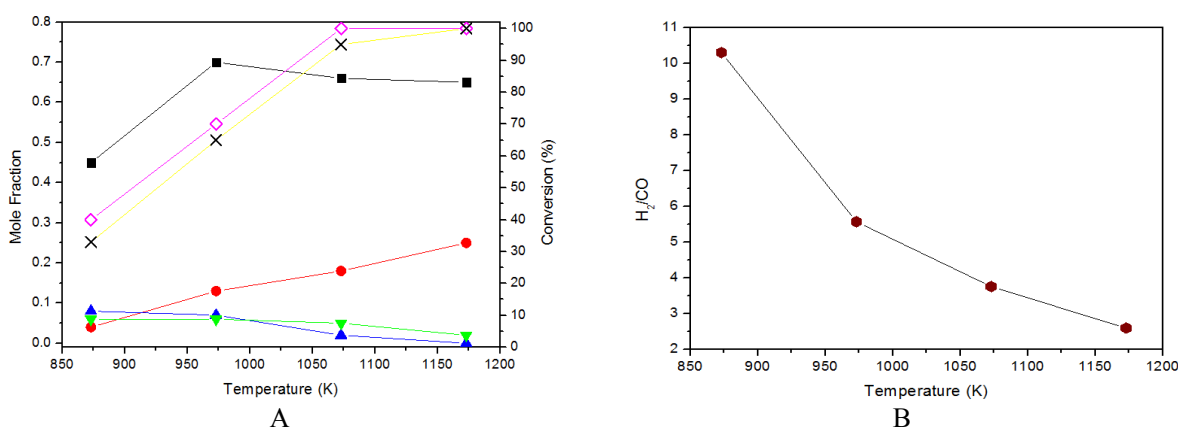


Figure 3: Experimental Data: C_4H_{10} and C_3H_8 conversions, mole fractions and H_2/CO ratio (Conditions: $H_2O/LPG = 3.5/0.5C_4H_{10}-0.5C_3H_8$; $W/F=0.05$ mg.min. L^{-1}) as a function of temperature.
 ■ Y_{H_2} ; ● Y_{CO} ; ▲ Y_{CH_4} ; ▼ Y_{CO_2} ; ◆ C_4H_{10} Conversion; × C_3H_8 Conversion

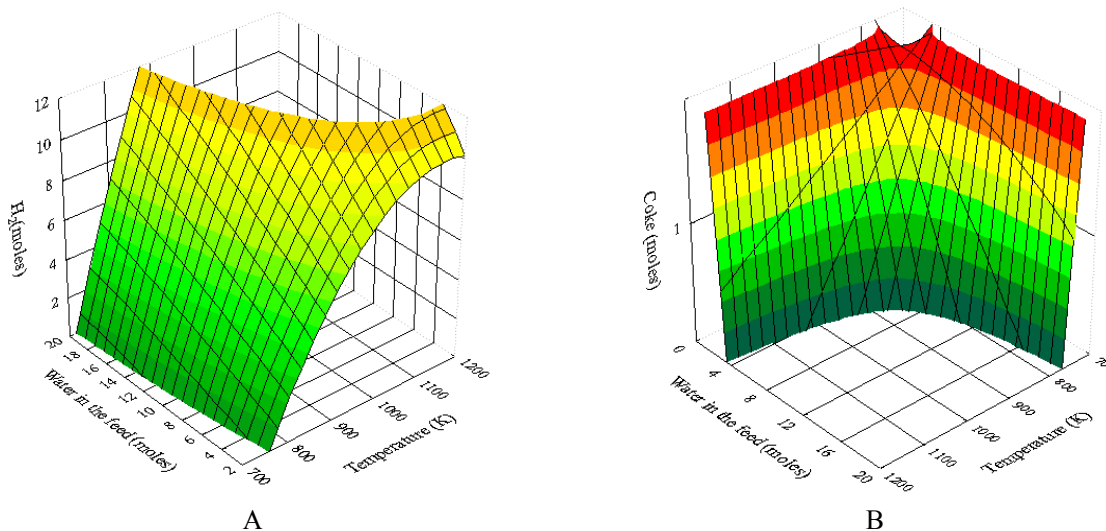


Figure 4: Number of moles of H_2 and coke calculated at equilibrium as a function of temperature and number of moles of water fed.

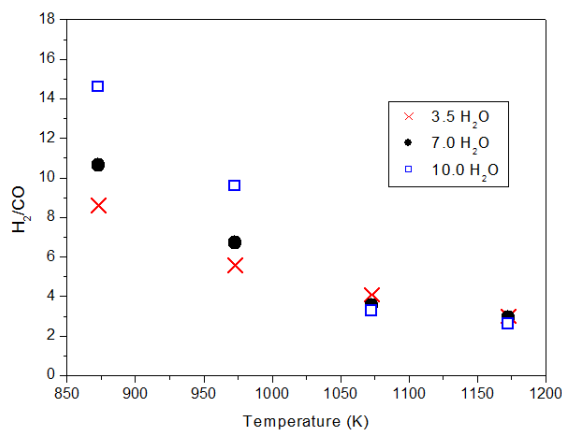


Figure 5: Effect of excess water on H_2/CO ratio obtained experimentally in the steam reforming of LPG as a function of temperature (Conditions: $0.5C_4H_{10}-0.5C_3H_8$; $W/F = 0.05 \text{ mg} \cdot \text{min} \cdot \text{L}^{-1}$).

Figure 6 shows the experimental H_2 mole fraction on a dry basis and conversion of butane and propane obtained from the steam reforming of LPG (A: $H_2O/LPG = 3.5$; B: $H_2O/LPG = 7.0$; C: $H_2O/LPG = 10$; $W/F = 0.05 \text{ mg} \cdot \text{min} \cdot \text{L}^{-1}$). The reactions were carried out at different temperatures: 873, 973, 1073 and 1173 K. Note that, regardless of the feed, the temperature increase generates an increase in the conversions of propane and butane. Furthermore, the use of a higher H_2O/LPG ratio generated an increase in conversion. Similar results were observed by Rostrup-Nielsen and Sehested (2002) for the steam reforming of methane: the use of high steam/hydrocarbon ratios (4-5 moles of H_2O per carbon atom) resulted in high hydrocarbon conversions.

The data obtained at 873 K (Figure 6A) also show that the H_2 mole fraction began around 0.45 and de-

creased strongly (~ 0.26) during the 6 hours of reaction. At 973 K, there is an initial increase in this variable (~ 0.69). However, after approximately 2 hours of reaction, there is a decrease in the H_2 mole fraction. According to Laosiripojana and Assabumrungrat (2006), milder temperatures favor the decomposition of butane and propane and the final state is the production of C^* and CH_4 . The resulting C^* species can react with oxygen species from the dissociation of water, or remain adsorbed on the active sites, leading to deactivation of the catalyst. Therefore, at intermediate temperatures (873 and 973 K), it is possible that the formation of C^* species is privileged, thus justifying the strong catalytic deactivation. At 1073 K, we note that, during the 6 hours of reaction, the hydrogen mole fraction is initially lower than at 973 K and stable around 0.65.

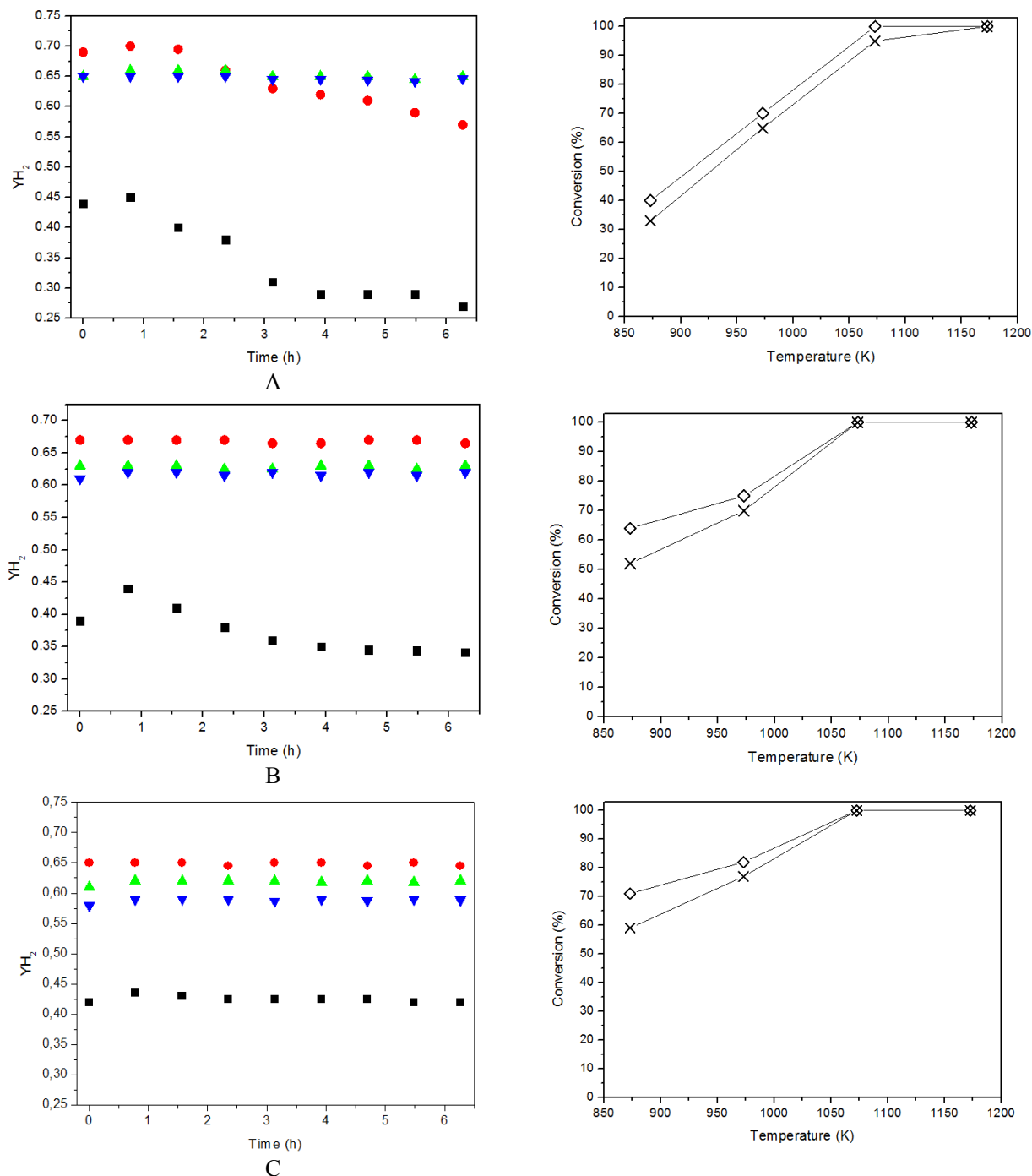


Figure 6: H₂ mole fraction on a dry basis and propane and butane conversions obtained during the steam reforming of LPG (A: H₂O/LPG = 3.5; B: H₂O/LPG = 7.0; C: H₂O/LPG = 10; W/F = 0.05 mg.min.L⁻¹). Y_{H₂}: ■ 873 K; ● 973 K; ▼ 1073 K; ▲ 1173 K; ◇ C₄H₁₀ conversion; × C₃H₈ conversion.

Starting from 1073 K, there is a large increase in the production of CO, which results in the decrease of the fraction of H₂ and stability of the reaction system. The stability observed in these data is directly related to the use of high temperatures, which results

in the removal of carbon deposits, causing a higher catalytic stability.

H₂ mole fractions obtained from the steam reforming of LPG using a molar ratio of H₂O/LPG equal to 7.0 are shown in Figure 6B. At 873 K, this

variable starts around 0.44, but decreases after 2 hours of reaction, indicating the deactivation of the catalyst. At 973 K, we observe stable values around 0.67 for H₂. This catalyst stability could be related to the addition of more water to the reaction system (H₂O/LPG = 7.0). At 1073 and 1173 K, the H₂ mole fraction is stable around 0.63. However, regardless of the temperature, when we compare Figures 6A-B, we note that the H₂ mole fraction is smaller for the system with the larger amount of steam. This happens because the larger quantity of water favors the formation of both CO and H₂. Thus, the increase in the number of moles of CO results in a decrease in the H₂ mole fraction for all temperatures analyzed. Similar results were observed by Zhu and coworkers (2010), who analyzed the production of hydrogen and synthesis gas in steam reforming of methane. According to these authors, the increased amount of vapor and temperature promote the increase in both H₂ and CO mole fractions.

The data obtained for the H₂ mole fraction for a H₂O/LPG ratio equal to 10 are shown in Figure 6C. Independent of the temperature analyzed, during the 6 hours of reaction, the H₂ yields were stable, indicating that excess water favors the catalytic stability. At temperatures above 973 K, the values of the H₂ mole fraction are larger in comparison to the lowest temperature (873 K). Another interesting fact is that, regardless of the amount of water added to the system (Figures 7A-C), the mole fraction of H₂ was higher at 973 K. However, stable and high values of H₂ mole fractions were obtained when using a ratio H₂O/LPG = 7.0. This is an indication that the temperature of 973K and ratio H₂O/LPG= 7.0 are the most appropriate conditions for this process. Similar results were thermodynamically predicted by Wang and coworkers (2010), who analyzed the best operating conditions for the reactions of steam and dry reforming of propane. According to these authors, in relation to the amount of hydrogen obtained in the steam reforming of propane, the number of moles of H₂ increases steadily with increasing temperature when the ratio H₂O/C₃H₈ is less than 6.

It is important to consider that the addition of excess water should be considered carefully because it is related to the operating cost of the process. The effect of the addition of excess steam at different temperatures on the energy demand for the steam reform of LPG is presented in Table 5. This table shows the energy demand required to operate the system with 3.5, 7.0 and 10.0 moles of water at temperatures ranging from 873 to 1073 K. The temperature increase causes an increase in energy demand, independent of the amount of water used, leading to

higher operating costs. Experimentally, it was observed that the most appropriate operating conditions to obtain H₂ from steam reforming of LPG were: T = 973 K and H₂O/LPG = 7.0. Table 5 shows that, under these experimental conditions, the operating costs are intermediate, which can facilitate the industrial implementation of these operational conditions.

Table 5: Energy demand to operate the system as a function of the water added.

Temperature (K)	Energy Demand (kJ/mol HC)		
	Water (moles) per mol of Hydrocarbon		
	3.5	7.0	10.0
873	307.90	534.95	728.71
973	341.29	582.52	788.17
1073	376.18	631.41	849.3
1173	412.41	682.82	913.31

Comparison Between Thermodynamic and Experimental Oxidative Reforming of LPG System

The addition of oxygen to the system can be a good choice to try to decrease the amount of solid carbon that is generated mainly in systems with higher hydrocarbons. According to Ayabe and coworkers (2003), oxidative reforming, which is the combination of the reactions of steam reforming and partial oxidation, may cause a decrease in the amount of coke generated.

Table 6 presents the equilibrium constants for all the reactions of oxidative reforming of the LPG system calculated at different temperatures (873 to 1173 K). Reactions 4.1, 4.2, 4.3, 4.4, 4.5 are endothermic, while reactions 4.6 and 4.7 are exothermic. Reaction 4.8 represents the addition of oxygen to the oxidative reforming system, which is an exothermic reaction.

Table 6: Equilibrium constants for the reactions considered in the oxidative reforming of LPG as a function of temperature.

	873 K	973 K	1073 K	1173 K
K1	2.398 x 10 ³	2.358 x 10 ⁴	1.517 x 10 ⁵	7.097 x 10 ⁵
K2	2.236 x 10 ³	2.198 x 10 ⁴	1.412 x 10 ⁵	6.596 x 10 ⁵
K3	1.060 x 10 ⁴	9.081 x 10 ⁴	5.225 x 10 ⁵	2.230 x 10 ⁶
K4	3.466 x 10 ⁵	3.899 x 10 ⁵	4.287 x 10 ⁵	4.630 x 10 ⁵
K5	5.092 x 10 ⁻¹	1.218 x 10 ¹	1.636 x 10 ²	1.424 x 10 ³
K6	2.710 x 10 ⁰	1.641 x 10 ⁰	1.104 x 10 ⁰	8.018 x 10 ⁻¹
K7	4.313 x 10 ⁰	6.284 x 10 ⁻¹	1.308 x 10 ⁻¹	3.550 x 10 ⁻²
K8	8.814 x 10 ¹¹	2.701 x 10 ¹⁰	1.532 x 10 ⁹	1.434 x 10 ⁸

Figure 7A illustrates the number of moles of hydrogen obtained at equilibrium for different amounts of water in the feed (H₂O/0.5C₄H₁₀-0.5C₃H₈/O₂)

necessary to obtain 1% or less of carbon deposition for the oxidative reform of LPG. The hydrocarbon to oxygen ratio in the feed was $0.5C_4H_{10}-0.5C_3H_8 / 0.25$. Compared to Figure 4A, the addition of oxygen generated a small increase in hydrogen yield, independent of temperature and the amount of water used. This result is in agreement with the literature (Ayabe *et al.*, 2003; Gokaliler *et al.*, 2008). Figure 7B presents the number of moles of solid carbon obtained in these same conditions. Independent of temperature and the amount of water used, the addition of oxygen led to lower coke formation, as predicted in various studies in the literature (Faria *et al.*, 2008; Li *et al.*, 2008).

Figure 8 compares experimental and equilibrium data for H_2 and CO mole fractions obtained for LPG oxidative reforming as a function of temperature. The conditions used were: $H_2O/LPG/O_2 = 7/1/0.25$, $W/F = 0.05 \text{ mg.mL.L}^{-1}$, $T = 873, 973, 1073$ and 1173 K . In general, the addition of oxygen to the system resulted in an increase in the H_2 mole fraction in both experimental and equilibrium conditions, especially at 873 K where there is a high coke formation. Similar theoretical results were obtained by Zeng and coworkers (2010), who evaluated thermodynamically the oxidative reforming of propane. According to these authors, in cases where the addition of oxygen occurs, there is an increase in the total energy of

the system, which consequently causes the promotion of carbon consumption reactions. However, experimentally even with the addition of oxygen, it was not possible to avoid the deactivation process at 873 K. This deactivation is related to coke formation.

Increasing the temperature to 973 K, the H_2 mole fraction increases and reaches higher values than predicted by the equilibrium calculation. This happens because, in this temperature range, there is a real increase in the number of moles of hydrogen due to the temperature increase. Furthermore, the amount of CO obtained experimentally is much lower than that predicted by thermodynamic analysis. This fact is an indication that the carbon-containing species obtained by the cleavage of butane and propane (CH_4 and C^*) are not being fully converted to CO (or CO_2) and H_2 . In fact, the H_2 mole fraction obtained in both equilibrium and experimental conditions at 1073 K and 1173 K are lower than those obtained at 973 K. Thus, it can be generally concluded that the use of a ratio of $H_2O/LPG/O_2 = 7.0/1.0/0.25$ and $T = 973 \text{ K}$ is the most suitable condition for the production of H_2 from LPG. This is because the excess water favors the formation of hydrogen with an intermediate operating cost and the addition of a small amount of oxygen promotes the removal of carbon deposits, contributing to the catalytic stability.

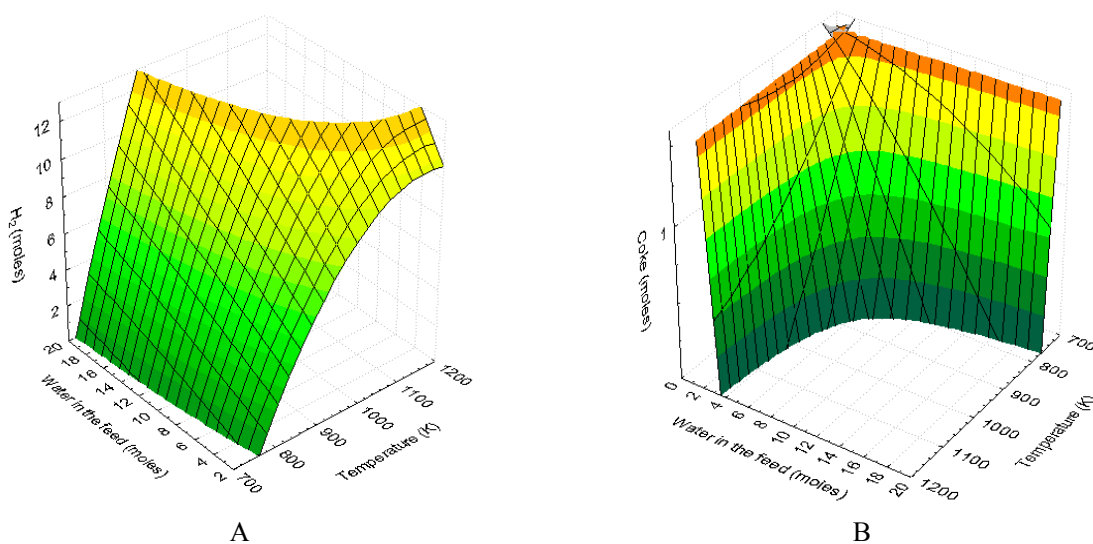


Figure 7: H_2 Mole fraction and number of moles of coke calculated at equilibrium conditions as a function of temperature and amount of water in the feed (Considering a feed of 0.5 moles of propane and 0.5 moles of butane and 0.25 moles of oxygen).

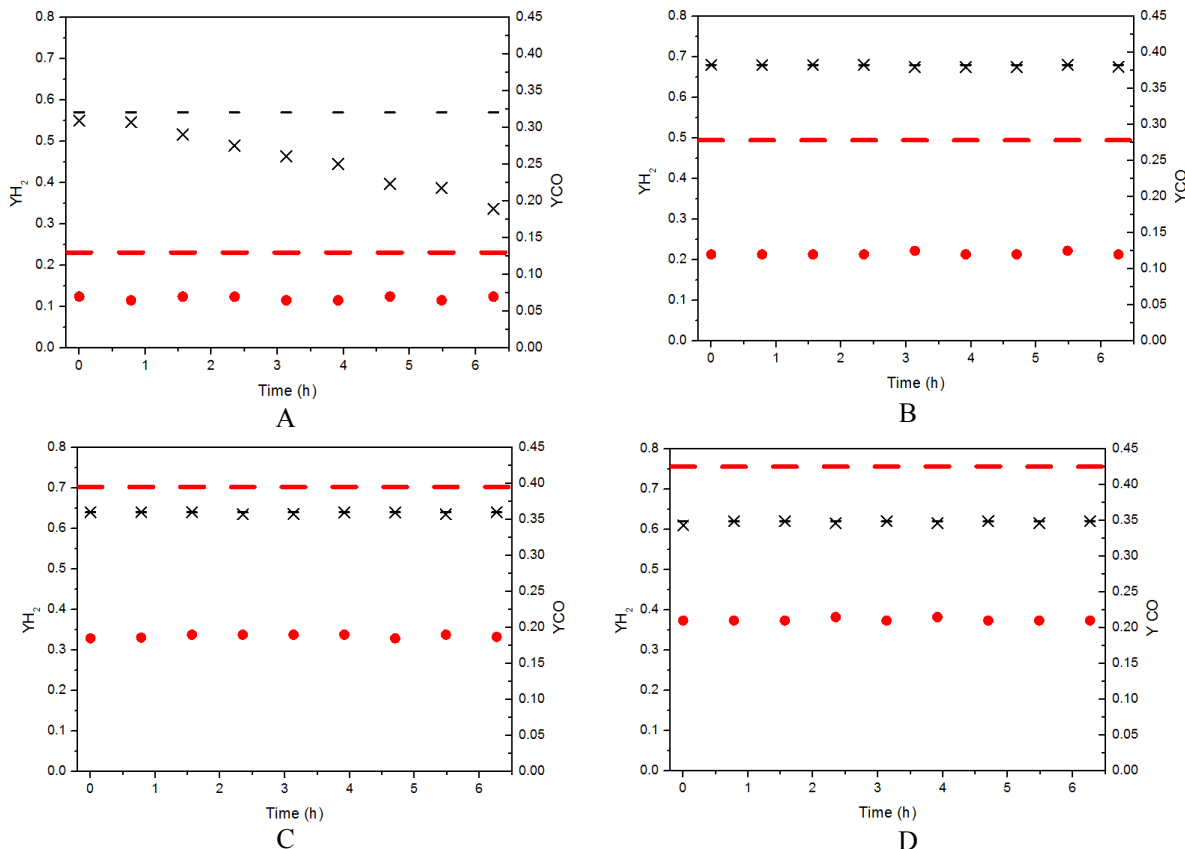


Figure 8: Comparison between H_2 and CO mole fractions obtained experimentally during the oxidative reforming of LPG and the calculated equilibrium data. (Conditions: $H_2O/LPG/O_2 = 7.0/1.0/0.25$; $W/F = 0.05 \text{ mg} \cdot \text{min} \cdot L^{-1}$).

A: 873 K, B: 973 K, C: 1073 K, D: 1173 K).

× Y_{H_2} Experimental; — Y_{H_2} Equilibrium; ● Y_{CO} Experimental; — Y_{CO} Equilibrium

CONCLUSIONS

From this work, it can be concluded that it is possible to produce high concentrations of hydrogen from LPG reforming. The gradual increase of temperature and the use of high water concentrations decrease the production of coke and increase the formation of H_2 . In this system, the final state of propane and butane cleavage is the production of C^* and H_2 . The reaction of oxidative reforming of LPG was more suitable for the production of hydrogen and lower coke formation. Furthermore, excess water ($H_2O/LPG = 7.0$) and intermediate temperatures (973 K) are the most suitable conditions for the process.

ACKNOWLEDGMENTS

The authors wish to acknowledge FAPEMIG, CAPES and CNPq for the financial support.

REFERENCES

- Ahmed, S., Krumpelt, M., Hydrogen from hydrocarbon fuels for fuel cells. *International Journal of Hydrogen Energy*, 26, 291-301 (2001).
- Avcı, A. K., Trimm, D. L., Aksoylu, A. E., Onsan, Z. I., Hydrogen production by steam reforming of n-butane over supported Ni and Pt-Ni catalysts. *Applied Catalysis A: General*, 258, 235-240 (2004).
- Ayabe, S., Omoto, H., Utaka, T., Kikuchi, R., Sasaki, K., Teraoka, Y., Eguchi, K., Catalytic autothermal reforming of methane and propane over supported metal catalysts. *Applied Catalysis A: General*, 241, 261-269 (2003).
- Barreto, L., Makihira, A., Riahi, K., The hydrogen economy in the 21st Century: A sustainable development scenario. *International Journal of Hydrogen Energy*, 28, 267-284 (2003).
- Cheekatamarla, P. K., Finnerty, C. M., Reforming catalysts for hydrogen generation in fuel cell

- applications. *Journal of Power Sources*, 160, 490-499 (2006).
- Corbo, P., Migliardini, F., Hydrogen production by catalytic partial oxidation of methane and propane on Ni and Pt catalysts. *International Journal of Hydrogen Energy*, 32, 55-66 (2007).
- Dantas, S. C., Resende, K. A., Rossi, R. L., Assis, A. J., Hori, C. E., Hydrogen production from oxidative reforming of methane on supported nickel catalysts: An experimental and modeling study. *Chemical Engineering Journal*, 197, 407-413 (2012).
- Dias, J. A. C., Assaf, J. M., Autothermal reforming of methane over Ni/ γ -Al₂O₃ catalysts: The enhancement effect of small quantities of noble metals. *Journal of Power Sources*, 130, 106-110 (2004).
- Díaz Alvarado, F., Garcia, F., Steam reforming of ethanol for hydrogen production: Thermodynamic analysis including different carbon deposits representation. *Chemical Engineering Journal*, 165, 649-657 (2010).
- Faria, W. L. S., Dieguez, L. C., Schmal, M., Autothermal reforming of propane for hydrogen production over Pd/CeO₂/Al₂O₃ catalysts. *Applied Catalysis B: Environmental*, 85, 77-85 (2008).
- Ferradon, M., Kropf, A. J., Krause, T., Bimetallic Ni-Rh catalysts with low amounts of Rh for the steam and autothermal reforming of n-butane for fuel cell applications. *Applied Catalysis A: General*, 122, 1-8 (2010).
- Gokaliler, F., Çaglayan, B. S., Onsan, Z. I., Aksoylu, A. E., Hydrogen production by autothermal reforming of LPG for PEM fuel cell applications. *International Journal of Hydrogen Energy*, 33, 1383-1391 (2008).
- Jeong, H., Kang, M., Hydrogen production from butane steam reforming over Ni/Ag loaded MgAl₂O₄ catalyst. *Applied Catalysis B: Environmental*, 95, 446-455 (2010).
- Laosiripojana, N., Assabumrungrat, S., Hydrogen production from steam and autothermal reforming of LPG over high surface area ceria. *Journal of Power Sources*, 158, 1348-1357 (2006).
- Laosiripojana, N., Sutthisripok, W., Charojrochkul, S., Assabumrungrat, S., Steam reforming of LPG over Ni and Rh supported on Gd-CeO₂ and Al₂O₃: Effect of support and feed composition. *Fuel*, 90, 136-141 (2011).
- Laosiripojana, N., Sutthisripok, W., Kim-Lohsoontorn, P., Assabumrungrat, S., Reactivity of Ce-ZrO₂ (doped with La-, Gd-, Nb-, and Sm-) toward partial oxidation of liquefied petroleum gas: Its application for sequential partial oxidation/steam reforming. *International Journal of Hydrogen Energy*, 35, 1-10 (2010).
- Li, M., Wang, X., Li, S., Wang, S., Ma, X., Hydrogen production from ethanol steam reforming over nickel based catalysts derived from Ni/Mg/Al hydrotalcite like compounds. *International Journal of Hydrogen Energy*, 35, 6699-6708 (2010).
- Li, Y., Wang, Y., Zhang, X., Mi, Z., Thermodynamic analysis of autothermal steam and CO₂ reforming of methane. *International Journal of Hydrogen Energy*, 33, 2507-2514 (2008).
- Lima, S. M., Silva, A. M., Costa, L. O. O., Assaf, J. M., Jacobs, G., Davis, B. H., Mattos, L. V., Noronha, F. B., Evaluation of the performance of Ni/La₂O₃ catalyst prepared from LaNiO₃ perovskite-type oxides for the production of hydrogen through steam reforming and oxidative steam reforming of ethanol. *Applied Catalysis A: General*, 377, 181-190 (2010).
- Montané, D., Bolshak, E., Abelló, S., Thermodynamic analysis of fuel processors based on catalytic-wall reactors and membrane systems for ethanol steam reforming. *Chemical Engineering Journal*, 175, 519-533 (2011).
- Moon, D. J., Hydrogen production by catalytic reforming of gaseous hydrocarbons (methane & LPG). *Catalysis Surv. Asia*, 12, 188-202 (2008).
- Rossi, C. C. R. S., Alonso, C. G., Antunes, O. A. C., Guirardello, R., Cardozo-Filho, L., Thermodynamic analysis of steam reforming of ethanol and glycerine for hydrogen production. *International Journal of Hydrogen Energy*, 34, 323-332 (2009).
- Rostrup-Nielsen, J. R., Sehested, J., Hydrogen and synthesis gas by steam- and CO₂ reforming. *Advances in Catalysis*, 47, 65-139 (2002).
- Silberova, B., Venvki, H. J., Holmen, A., Production of hydrogen by short contact time partial oxidation and oxidative steam reforming of propane. *Catalysis Today*, 99, 69-76 (2005).
- Smith, J. M., Van Ness, H. C., Abbott, M. M., Introduction for Chemical Engineering Thermodynamics. 7th Ed., McGraw-Hill Science Engineering (2007).
- Walas, S. M., Phase Equilibria in Chemical Engineering. Butterworth-Heinemann, Boston, (1985).
- Wang, X., Wang, N., Wang, L., Hydrogen production by sorption enhanced steam reforming of propane: A thermodynamic investigation. *International Journal of Hydrogen Energy*, 36, 466-472 (2011).
- Wang, X., Wang, N., Zhao, J., Wang, L., Thermodynamic analysis of propane dry and steam reforming for synthesis gas or hydrogen production. *International Journal of Hydrogen Energy*, 35,

- 12800-12807 (2010).
- Zeng, G., Tian, Y., Li, Y., Thermodynamic analysis of hydrogen production for fuel cell via oxidative steam reforming of propane. *International Journal of Hydrogen Energy*, 35, 6726-6737 (2010).
- Zhu, X., Wang, H., Wei, Y., Li, K., Cheng, X., Hydrogen and syngas production from two-step steam reforming of methane over $\text{CeO}_2\text{-Fe}_2\text{O}_3$ oxygen carrier. *Journal of Rare Earths*, 28, 907-924 (2010).